CARBONATE SURFACE CHEMISTRY: EFFECT OF MONOVALENT IONS

BY

AHMED SADEED

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This thesis, written by **AHMED SADEED** under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN PETROLEUM ENGINEERING.**

Dr. HASAN S. AL-HASHIM
(Advisor)

Dr. ABDULLAH S. SULTAN
Department Chairman

Dr. WAEL ABDALLAH
(Co-Advisor)

Dr. Salam A. Zummo
Dean of Graduate Studies

Dr. HASAN AL-YOUSEF
(Member)

1/6/17
Date

Dr. ABDULLAH S. SULTAN
(Member)

Dr. FAIZ UR RAHMAN
(Member)

Dedication

I dedicate this effort to my mother; the reason of my success in every step of my life.

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All praise to the Almighty for his countless blessings bestowed upon me and giving me the strength to complete this work. Without His help, nothing is possible. No words of thanks are enough to express my gratitude towards him.

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LIST OF ABBREVIATIONS

EOR	:	Enhanced Oil Recovery
IOR	:	Improved Oil Recovery
LoSAL	:	Low salinity
LSF	:	Low salinity water flooding
SEM	:	Scanning Electron Microscope
XRD	:	X-Ray Diffraction
XRF	:	X-Ray Fluorescence
IFT	:	Interfacial Tension
NMR	:	Nuclear Magnetic Resonance
FTIR	:	Fourier transform infrared spectroscopy
AFM	:	Atomic Force Microscopy
ICP-OES	:	Inductively Coupled Plasma-Optical Emission Spectrometry
AN	:	Acid Number
BN	:	Base Number

I.S	:	Ionic Strength
OOIP	:	Original Oil in Place
DI	:	De-Ionized Water
FW	:	Formation Water
SW	:	Sea Water

ABSTRACT

Full Name : Ahmed Sadeed

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Carbonate reservoirs rocks have been characterized to be neutral to oil wet rocks. Smart water flooding or Low salinity flooding have shown great potential for modifying carbonate rock wettability to more water wet condition and consequently leading to incremental oil recovery.

Smart water or low salinity water flooding at the lab scale revealed significant incremental oil recovery. This was supported by very promising results from field trials. Identification of the mechanism leading to the incremental oil recovery have been of great interest to many researchers. This can be seen from the published technical papers during the past twenty years. Wettability alteration has been reported as one of the mechanism leading to the incremental oil recovery. However, what is causing this wettability alteration to more water wet condition is not fully understood. Even though several ions have been proposed to be potential determining ions such as Ca^{2+}, Mg^{2+} and SO_4^{2-}, the role of other ions cannot be ruled out. Because of the positively charged carbonate rock surface in high saline formation water, in this study, we are investigating the role of anions in the injected brines to stimulate interactions with the carbonate surface. Two different carbonate rocks: Calcite

and Carbonate outcrop are used in this study. The calcite rock (approx. 100 % $CaCO_3$) is used to serve as a basis under controlled system. This is necessary to evaluate the impact of the other anions on calcium carbonate which composes more than 90% of the carbonate rock. In this study, we are interested in modifying the sea water composition rather than diluting it by adding an acceptable amount of anions to enhance the rock/fluid interactions and consequently altering the carbonate rock wettability to a more water wet condition. Furthermore, performed experiments using DI water, so in this way, we can differentiate the behavior of both rocks either unmodified or modified with different model oils.

The prime focus of the study is to investigate the effect of monovalent anions (Cl^-, Br^- and I^-) on the carbonate rock surface charges. Single salt solutions of NaCl, NaBr and NaI in deionized water with equal salinity of 5000 ppm each, were used to analyze the effect of anions on the calcite and carbonate outcrop rock surfaces. Synthetic Arabian Gulf sea water (~57000ppm) and synthetic sea water with added single salt (NaCl, NaBr and NaI) were also used to examine the surface rock changes at high salinity. Three model oils: stearic acid and/or asphaltene dissolved in toluene were used to represent the oil phase and to prepare modified or oil wet samples. Rock surface charges alteration were determined by zeta potential measurements and supported by surface characterization technique, such as SEM-EDS.

Zeta potential of calcite and carbonate outcrop is negative in DI water due to preferential leaching of Ca^{2+} ions from the calcium carbonate lattice. The magnitude of negative zeta potential is high in carbonate outcrop used in this study as compared to calcite due to the presence of silica content in carbonate outcrop rock. The magnitude of negative zeta potential in calcite rock increase when the rock is aged with the model oils and suspended

in DI water, as compared to unmodified calcite rock suspensions in DI water. This is due to the adsorption of surface active components from the model oils onto the rock surface. Thus, the increase in negative zeta potential indicates that the calcite rock particles are altered to oil wet. The magnitude of zeta potential values of calcite rock aged in different model oils and suspended in DI water are all similar. This is due to the competition between stearic acid and asphaltene to adsorb on the limited sites of calcite surface and the effect of stearic acid and asphaltene is not added up. 5000 ppm NaI and 5000 ppm NaBr both showed consistent less negative charge on the rock surfaces in all modified calcite rocks as compared to modified calcite rocks in DI water. All low salinity brines showed less negative charge for carbonate outcrop rock modified with stearic acid as compared to corresponding values in DI water, while 5000 ppm NaBr showed the least negative charge. This is due to the desorption of adsorbed model oil component (stearic acid) that was causing the increased negative charge.

Addition of 5000 ppm NaI or NaBr in Sea water is found to be good alternative in releasing polar oil components from the rock surface. Whereas, SW0.5%NaI showed more promising results as compared to SW0.5%NaBr. The release of adsorbed oil from the rock surface alter the rock surface from strong oil wet to less oil wet and consequently, leads to incremental oil recovery.

ملخص الرسالة

الإسم : أحمد سديد

عنوان الرسالة : كيمياء الصخور الجيرية: تأثير ايونات احادية التكافؤ

التخصص : هندسة البترول

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اتسمت الصخور الكربونية بأن تكون محايدة للصخور النفطية الرطبة بالماء. وأظهر إستخدام آليات smart water flooding و Low Salinity flooding إمكانيات كبيرة لتعديل قابلية ترسب الصخور الكربونية إلى المزيد من حالة قابلية التبلل (wettability).

وكشفت smart water flooding و Low Salinity flooding على مستوى المختبر عن زيادة كبيرة في إستخراج النفط. وأيد ذلك نتائج واعدة جدا من التجارب الميدانية. وقد كان تحديد الآلية المؤدية إلى الإستخراج التدريجي للنفط ذا أهمية كبيرة لكثير من الباحثين. ويمكن رؤية ذلك من الأوراق البحثية التقنية المنشورة خلال العشرين عاما الماضية. أظهرت تلك الأبحاث عن تغير قابلية البلل (wettability) باعتبارها واحدة من الآليات المؤدية إلى الإستخراج التدريجي للنفط. ومع ذلك، فإن الأسباب في هذا التغيير في قابلية البلل (wettability) إلى المزيد في حالة المياه الرطب غير مفهومة تماما. مع ان هناك بعض الايوانات التي يمكن استخدمها لتحديد الايونات مثل Ca^{2+}, Mg^{2+} and SO_4^2 ، لكن لا يمكن تجاهل دور تلك الايونات كليا.

وللصخور الكربونية سطح مشحون إيجابيا في المتكونات الصخرية ذات المياه المالحة. وهذا هو السبب في أننا مهتمون في الأنيونات في المحاليل الملحية في حقنها لتعطي تفاعلا أفضل مع سطح الكربونات. في هذه الدراسة، استخدمنا اثنين من الصخور الكربونية المختلفة: صخر الكالسيت والصخر الكربوني. إستخدمنا صخور الكالسيت (حوالي 100٪ من $CaCO_3$) للحصول على تحكم أفضل في نظامنا. اضافة نظام التحكم ايضا مهما لنا لكي نستطيع تقييم تأثير الايونات على كاليسيوم كاربونات الذي يشكل 90% من الصخور الجيرية. في هذه الدراسة، نحن مهتمون بتعديل تركيب مياه

البحر بدلا من تميعيها باضافة كمية من الايونات للتعزيز التفاعل بين الصخور و السوائل. هذا سوف يساعدنا في تعديل قابلية ترسب الصخور الكربونية إلى المزيد من حالة قابلية التبلل (wettability). أجرينا أيضا تجارب باستخدام مياه داي (DI Water)، وذلك بهذه الطريقة، يمكننا التفريق بين سلوك كل من الصخور إما غير معدلة أو معدلة مع عينات الزيت المختلفة.

التركيز الرئيسي للدراسة هو دراسة تأثير الأنيونات أحادية التكافؤ (Cl^-، Br^- أو I^-) على سطح صخور الكربونات. لذلك الغرض تم استخدام محاليل ملح مفردة من كلوريد الصوديوم NaCl, NaBr and NaI في الماء منزوع الأيونات مع ملوحة متساوية من 5000 جزء في المليون لكل منهما لتحليل تأثير الأنيونات على السطوح الصخرية الكالسيت والكربونات الصخرية. كما تم استخدام مياه مصنعة ذات ملوحة مماثلة لمياه الخليج العربي (~ 57000ppm) ومياه مصنعة مع إضافة ملح واحد (NaCl, NaBr and NaI) لدراسة التغيرات الصخرية السطحية في الملوحة العالية. تم استخدام ثلاثة زيوت نموذجية: حامض دهني و / أو أسفالتن المذاب في التولوين لتمثيل مرحلة الزيت وإعداد عينات معدلة أو زيتية مبللة. تم تحديد تغيير رسوم سطح الصخور بواسطة قياسات زيتا المحتملة وبدعم من تقنية توصيف السطح، مثل سيم-إدس.

النتائج المحتمل الحصول عليها من قياسات زيتا من الكالسيت والصخر الكربوني هو سلبي في مياه داي (DI Water) بسبب الترشيح لأيونات Ca^{2+} من كربونات الكالسيوم. محصلة قدرة زيتا السلبية عالية في الصخر الكربوني بالمقارنة مع الكالسيت، والذي يرجع إلى وجود محتوى السيليكا في الصخور الكربونية المستخدمة. محصلة قدرة زيتا السلبية لصخر الكالسيت تزداد معا زيادة عمر الصخور المضاف إليه عينات الزيوت بعد غمره في مياه داي، بالمقارنة مع غمر صخور الكالسيت غير المعدلة في مياه داي. ويرجع ذلك إلى امتصاص المكونات النشطة السطحية من عينات الزيوت على سطح الصخور. وهكذا، فإن الزيادة في قدرة زيتا السلبية تشير إلى أن جزيئات صخور الكالسيت تغيرت إلى النفط الرطب المشبع بالماء. حجم القيم المحتملة لقياسات زيتا من صخور الكالسيت المختلفة بإختلاف عينات الزيت المستخدمة معا كل عينة ومغمورة في مياه داي كلها مماثلة. ويرجع ذلك إلى المنافسة بين الحامض دهني و أسفالتن لامتصاص على مواقع محدودة من سطح الكالسيت وتأثير الحمض دهني و أسفالتين لا تضيف ما يصل. 5000 جزء في المليون NaI و 5000 جزء في المليون NaBr على حد سواء أظهرت ثبات أقل في شحنة السلبية على الأسطح

الصخرية في جميع الصخور الكالسيت المعدلة بالمقارنة مع الصخور الكالسيت المعدلة في مياه داي. وأظهرت جميع المحاليل الملحية منخفضة الملوحة أقل شحنة سلبية للصخور الكربونية تعديل مع حامض دهني بالمقارنة مع القيم المقابلة في مياه داي، في حين أن 5000 جزء في المليون NaBr أظهرت أقل شحنة سلبية. ويرجع ذلك إلى الامتزاز من عنصر عينة النفط الممتص (حامض دهني) التي كانت تسبب زيادة الشحنة السلبية.

إضافة إلى 5000 جزء في المليون NaI أوNaBr في مياه البحر وجد أن يكون أفضل بديل في الإفراج عن مكونات النفط القطبية من سطح الصخور. في حين، أظهرت SW0.5%NaI نتائج أكثر واعدة بالمقارنة مع SW0.5%NaBr. ويؤدي الافراج عن الزيت الممتص من سطح الصخور إلى تغيير سطح الصخور من الزيت القوي الرطب إلى كميات أقل من الزيت الرطب، وبالتالي يؤدي إلى زيادة انتاج الزيت تدريجيا.

CHAPTER 1

INTRODUCTION

1.1 Overview

In the past two decades, the phenomenon of low salinity water flooding has been widely discussed and evaluated. The need of smart water has been increased due to its low capital and operating expenses as compared to other EOR methods. Several years of research and observations have shown potential in this new technology. In 1967, Bernard [1] first identified that low salinity water could improve the oil recovery. He used two types of sandstone cores that contained different percentages of clays and showed that oil recovery was higher when the samples were flooded with freshwater. In 2004, Webb [2] published the results of a single well test in sandstone formation with average porosity of 20% and permeability ranged from 200-700md. They conducted the log-inject log test on a single well to determine the residual oil saturation near the well after injecting the treated brine. In 2010, Seccombe et al. [3] published the result of the first inter-well field trial for sandstone reservoir. In 2012, Yousef et al. [4] reported the successful smart water field trials on carbonate reservoir. A reduction of 6 and 7 units in residual oil saturation, separately in two wells was observed as compared to conventional water flooding. The field trials showed a potential of smart water for enhanced oil recovery.

Many researchers proposed some mechanisms to explain the increased in oil recovery

during smart water flooding. The suggested mechanisms includes fines migration [5], [6], increase in pH leading to IFT reduction [7], [8], Multiple Ion Exchange [9]–[13] , double layer expansion [14]–[17] , Mineral dissolution [18] , and water micro dispersion [19] .

The research focus was mainly on sandstone until the unexpected high oil recovery observed upon injection of sea water into the fracture chalk reservoir of Ekofisk field [20].

Carbonate reservoirs exhibit 60% of the word oil reserves [21], [22] and usually characterized as low porosity and may be naturally fractured [23]. These two characteristics along with oil wet and mixed wet nature of carbonates [24] usually results in lower oil recovery as being 30% world average oil recovery for carbonates reported so far [23].

In highly saline formation water, the surface of carbonate rocks is positively charged due to high concentration of cations [25]. The adsorption of negatively charged polar components like carboxylic acids, $R\text{-}COO^-$ in the crude oil on to the positively charged carbonate surface makes the carbonate rock mixed wet or preferentially oil wet [26] . Medium-to-long chain fatty acids and carboxylate polymers are usually present in crude oils which have strong affinity to adsorb on carbonate minerals [27] due to availability of the carboxylic groups in these components which ionize and act similar to the carbonate anions of the mineral lattice. Carboxylic acids which are present in crude oil act as most crucial wetting parameter in carbonates [28] . Oil acidic components are quantified as Acid Number. Oil-wetness of the rock increases as the Acid Number (AN) of the crude oil increases [29] . As the reservoir temperature increases, the AN of the crude oil usually decrease due to decarboxylation. Therefore, as the reservoir temperature decreases, carbonate reservoir tends to be more oil wet [29]. At neutral pH, there is a positive charge present at the interface between carbonate and water due to high $[Ca^{2+}]$ in the formation

water and negatively charged interface is present between oil and water due to dissociation of carboxylic surface active material. Thus, due to attraction between opposite charges, the water film which is bound between rock/brine and brine/oil interface becomes unstable, and the oil make contact with the carbonate surface [30]. Existence of stable water films in a range of 1 to 100 nm thickness depends on the presence of electrical double-layer repulsion that results from surface charges at the solid/water and water/oil interfaces being of the same sign [9], [31] . In order to mobilize the retained oil by wettability and capillarity, capillary forces must be reduced [28].

It is generally accepted from reported publications that alteration of the injected water composition can alter rock wetting conditions and eventually improve oil recovery. This effect is generally related with the ion exchange between the key ions such as (SO_4^{2-}, Ca^{2+}, Mg^{2+}), also known as potential determining ions (PDIs) present in seawater and the minerals of the rock [32], [33]. As a result of alteration of rock surface charges due to injection of smart water, the carboxylic oil which is adsorbed on the carbonate surface desorbs, and consequently rock wettability is altered to less oil wet and more water wet condition.

1.2 Carbonate Mineralogy

Carbonate rocks consists of mainly carbonate minerals formed by the precipitation of organic or inorganic species from aqueous solution of calcium carbonates ($CaCO_3$) – limestone, or calcium plus magnesium ($CaMg(CO_3)_2$) – dolostone. The distinction between these two rocks is in percentage of different carbonates composing the rock. Limestones are composed of more than 50% $CaCO_3$. Dolomites are composed of more

than 50% $CaMg(CO_3)_2$. Most dolomites have formed by replacement of limestone, and the result is that in many cases the original structures are poorly preserved.

The common carbonates are characterized based on their crystal structure (the internal arrangement of atoms). There are three crystal systems exist in carbonates which are orthorhombic, hexagonal, and monoclinic crystallographic systems. Calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are the most common carbonate minerals which exists in the hexagonal system. The composition of aragonite is the same as calcite, $CaCO_3$, but when it crystallizes, it forms orthorhombic structure. Aragonite is rare in the ancient rocks that's why carbonate reservoirs are mainly composed of minerals calcite and dolomite — limestones and dolostones. These two rocks amount for about 90% of all naturally occurring carbonates.

1.3 Calcite

Calcite is the main constituent mineral including dolomite and anhydrite in the Middle East Carbonate (MEC) reservoirs. Calcite is found to be around 80% in MEC [34]. Calcite crystals are trigonal-rhombohedral which is similar to dolomite, though actual calcite rhombohedra are rare as natural crystals. However, the characteristics may vary including acute to obtuse rhombohedra, tabular forms, prisms, or various scalenohedra. Calcite may occur as fibrous, granular, lamellar, or compact. Its cleavage is usually in three directions parallel to the rhombohedron form. Its fracture is conchoidal.

Retrograde solubility is another characteristic of calcite in which as the temperature increases, the calcite becomes less soluble in water. When conditions are appropriate for precipitation, calcite acts as a cementing material and binds the grains of the rock together

or it could fill fractures as well. If dissolution occurs due to imbalance of chemical equilibrium, it can result in increased porosity and permeability due to the removal of calcite, and if the condition continues, it may eventually result in formation caving.

1.4 Problem Statement

Enhancing recovery factors in carbonate reservoirs is of critical importance to oil producers to meet future demand of oil consumptions; considering the fact carbonate recovery factors are low from the primary production and there haven't been much discoveries of new giant oil reservoir. To boost oil recovery, water flooding is widely used but it only produces 10-20% more oil and leave more than 50% of the original oil behind, therefore it is imperative to use other techniques such as chemical EOR and gas injection to recover it [35]. Most carbonate reservoirs are classified as mixed wet or preferentially oil wet with complex pore matrix [36]. As a result of this wettability and high capillary pressure, most of the conventional water flooding results are in the high residual oil saturation. In the last 10-15 years, the industry started to examine closely the effect of manipulating the injected water salinity and its ionic content to improve the recovery factors, techniques often called in the industry as Dynamic Water, Low Salinity Water, Smart Water, etc. It is believed such manipulation with the flooding water has a lower capital investment and operating cost, which makes it more attractive for the oil industry. That is true if you use available sea water with slight modification or if fresh water is available in great quantities, which is not the case in many areas such as Arabian Gulf area.

The biggest challenge in the Middle East is the availability of fresh water, to achieve low salinity, we either dilute sea water with fresh aquifer water or reduce the salinity of sea

water through distillation or reverse osmosis and in both of these methods, the cost of producing low salinity water is high which makes this low salinity process costly.

Extensive investigations have been carried out to tune the injected water composition and find out the characteristic parameters that help in designing it for specific reservoirs. As a result of these investigations, several recovery mechanisms have been proposed but not a single mechanism stands and able to provide the needed parameters that can help or direct us in designing the injected water. Our current interest in this area is to investigate the applicability of using the Arabian Gulf sea water (salinity of approx. 57,000 ppm) as the injected water with slight modification of its ionic content rather than diluting it; this option will be more economical. We aim to study the effect of monovalent anions addition to the injected water and examine closely their impact on rock surface properties using different characterization techniques.

This study focuses on addition of salts in sea water rather than sea water dilution. Dilution of sea water requires a huge capital investment for construction of desalination plant, a long time for construction and investment on facility to mix sea water with desalinated water. In order to reduce salinity of sea water down to 2 times or 10 times, it requires double or 10 times volume of fresh water. Also, if we do a simple cost analysis, we can observe that the average operating cost of desalination plant is 0.239 $/bbl [87]–[89] apart from large scale capital investment which varies between 0.3-15 billion dollars [87]. Whereas the cost of adding one gram sodium iodide and sodium bromide is approximately 0.159 $/bbl [90], [91]. Considering all these factors into account, we are now interested in addition of some specific salts in sea water which is more economical than sea water dilution.

1.5 Project Objective

The main objective of this research is to extend our knowledge and understanding of the impact of monovalent ions on the rock surface chemistry during water flooding.

The specific objectives are.

1.5.1 Investigate the role of individual monovalent ions such as Chloride, Bromide and Iodide on the surface charges of calcite and carbonate outcrop rock samples.

1.5.2 Investigate the role of monovalent ions added with sea water on the surface charges of calcite and carbonate rock samples.

1.5.3 Identify the ions adsorbed on the rock surface and desorbed from the rock surface when exposed to the different investigated brines used.

1.5.4 Quantify the changes in the composition of the rock surface

1.5.5 Identify the mechanism leading to the changes of the rock surface properties

1.6 Thesis Deliverables

The aim of this study is to investigate the role of monovalent ions on the surface changes of the carbonate rock. The results of this study will provide a new insight in the fundamentals of rock surface chemistry and will help in identifying the impact the individual ions on the rock surface. Without altering the original composition of sea water, monovalent ions will be added to the seawater original composition to investigate wettability alteration. It is generally believed that the wettability alteration and the incremental oil recovery occur when injecting low salinity water. However, in our case, the salinity of sea water would slightly increase and we are assuming that the effect of wettability alteration is not only dependent on low salinity water but it is the effect of individual ions as well that are present in the sea water.

1.7 Thesis Organization

In addition to the current chapter, this thesis consists of another three chapters. In chapter two, detailed literature review is given for major research on zeta potential and other means of microscopic surface characterization conducted to investigate oil recovery by smart water flooding. Chapter three summarizes all materials used in the current study in addition to a detailed description of all experimental procedures followed to achieve the objectives of the thesis. In chapter four, results are summarized and discussed in details. Chapter five summarizes our conclusions.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of the Mechanisms

Although, it has been widely accepted from laboratory experiments and field trials that smart water flooding results in incremental oil recovery, but how low salinity water flooding improves oil recovery in carbonate reservoirs is still not clear. The mechanisms that give rise to incremental oil recovery are not well understood. A review of the various explanations and controversies related to carbonate rock can be found in literature [37]. Table 1 presents highlights of the proposed mechanisms along with the contradictions on these proposed mechanisms.

Table 1: Suggested Mechanisms of low salinity of water flooding

Mechanism	Short Explanation	Contradiction
Multi Ion Exchange	SO_4^{2-} ions adsorb onto the positively charged carbonate surface and attract Ca^{2+} ions toward the surface thus release the negative charged polar oil component that is adsorbed on the rock surface as a calcium carboxylate complex. When temperature goes above 90^oC, Mg^{2+} is more active and	Increasing SO_4^{2-} did not increase oil recovery from spontaneous imbibitions and core flood experiments [38], [39].
		No additional recovery from core flood experiment by increasing temperature from 40 to 120^oC using seawater on reservoir chalk core [40].

	replace calcium ion from the surface.	Removal of NaCl from seawater yielded no extra oil production from spontaneous imbibition experiments on limestone [39], [41].
		The smart water flooding effect was also observed for injection and imbibing brines without PDIs (Ca^{2+} and Mg^{2+}, SO_4^{2-}) [39], [42], [43].
Rock Dissolution	Minerals such as huntite ($MgCa(CO_3)_4$), magnesite ($MgCO_3$), and anhydrite ($CaSO_4$) precipitate as magnesium- and/or sulfate-rich brine (e.g. seawater) is injected and calcite mineral dissolves to balance the aqueous concentrations of calcium and carbonate ions [44], [45]. Any polar oil compounds adsorbed on the dissolved mineral surface is released and exposing a water-wet surface. Oil recovery improves as dissolution increases pore system connectivity between macro- and micro-pores [46].	Diluted formation brine did not yield additional oil recovery even though the dissolution was certain as indicated by increase in Ca^{2+} in the effluent [18].
		In several core flooding and SI experiments on chalks and dolomites, no additional oil was recovered when injection or imbibing brine either bulk diluted or with reduced Ca^{2+} concentration was used [43], [47]–[49].
		Dolomite and limestone core floods yielded increased oil recovery but Ca^{2+} and Mg^{2+} in the effluent brine was the same as the injected seawater brines [43], [50].
		Introduction of seawater disturbs the formation brine-rock equilibrium and dissolution is hypothesized to occur only at water-wet sites [51], [52].
		Low salinity effect due to mineral dissolution may not occur at reservoir-scale because dissolution stops as diluted waterflood brine quickly becomes saturated with dissolved calcite [53].

Fine Migration	Plug pore throats due to mineral fines flow changes the direction of flow which improves the water sweep efficiency leading to improved oil recovery with increase in pressure drop. No fines production may be due to fines changing locations within the pore network. The precipitation of ions saturated in brine and/or detachment of mineral from the bulk mineral may form mineral fines [45], [50], [54].	The low salinity effect was observed without fines production and no increase in pressure drop at constant rate. [13], [55].
		Solubility studies are normally performed to avoid mineral precipitation. [13], [14], [50], [56].
		Mineral precipitation is observed to impede flow and reduce permeability leading to reduced oil production. [44], [57].
Double Layer Expansion (DLE)	Formation brines usually have high ionic strength, counterions are compacted in the diffuse layer by the high concentration of ions and its thickness is reduced. The electrical double layer expands due to the injection of low ionic strength brine which induces a diffusive gradient between the compacted counterions in the diffuse layer and bulk electrolyte. Due to DLE, binding forces of the bridging multivalent metal cations may be exceeding by the repulsive forces of the negatively charged oil and mineral surface causing polar oil components to desorb and expose a water-wet surface [14].	Carbonate mineral surface in the reservoir are generally believed to be positively charged at typical reservoir pH (< 9.5) and electrostatically attracts oil particles of opposite charge to adsorb on its surface [14], [58].
		The DLE theory cannot explain observations of improved oil recovery resulting from an increase in ionic strength as Ca^{2+}, Mg^{2+}, and/or SO_4^{2-} concentrations were increased [13], [59] or the absence of the low salinity effect in experiments where brine ionic strength was reduced [18], [48].

2.2 Recent Publications to Explain the Mechanism behind the Low Salinity Effect

Myint and Firoozabadi [60] presented a comprehensive study on the mechanisms involved in increased oil recovery from smart water flooding on sandstone and carbonate. They were focused on the wettability alteration mechanism that affects the interactions between brine/oil and brine/rock interfaces of thin brine film that wet the surface of reservoir rocks. They reviewed the recent studies on the wettability alteration mechanisms. For carbonates, they mentioned two mechanisms that alter wettability. These are double layer expansion and the chemical mechanism proposed by Austad and co-workers involving SO_4^{2-} produced by anhydrite dissolution. The chemical mechanism involves the dissolution of calcite and anhydrite minerals of carbonate rock to overcome the deficiency of concentrations of ions caused by the injection of low salinity brine. The dissolutions of calcite and anhydrite increase the pH and sulfate ion concentration, respectively. Both reactions cause the brine/oil surface to become negatively charged and repelled by the negatively charged brine/oil interface. The carbonate/brine interface may be further altered due to adsorption of ions, in the absence of dissolution. Consequently, the thin water film between interfaces becomes thicker which makes the rock water wet. The other mechanism proposed that, sulfate ions produced by anhydrite dissolution in low salinity water flood adsorbs to the carbonate surface. This leads to co-adsorption of Ca^{2+} and Mg^{2+} onto the rock. The Ca^{2+} ions can then react with carboxylic groups in oil that are bonded to the carbonate surface. The reaction with Ca^{2+} breaks the bonds between the brine/oil and brine/carbonate interfaces and causes release of the carboxylic groups, leading to improved oil recovery. At sufficiently high temperatures, Mg^{2+} can substitute Ca^{2+} on the carbonate surface and thereby displace Ca^{2+} ions on the surface that are bridged to carboxylic groups.

They supported the above mentioned theories with the results of experiments published by the researchers, mainly Yousef et al. during the recent past years that will be discussed later. They concluded that the work that has been done so far represents a qualitative analysis of low salinity wettability alteration and still the theories cannot explain all the observed results.

Nasralla et al. [61] conducted core flood experiments on two different limestone reservoir rocks from the Middle East. The rock from reservoir A was mainly calcite with little quartz and some traces of clay while reservoir B contained mainly calcite with little traces of quartz. Reservoir A oil has 0.1 mg KOH/g acid number while reservoir B oil has 0.38 mg KOH/g acid number. They used seven different brines. These were formation water of reservoir A (179,000 ppm), formation water of reservoir B (184,000 ppm), diluted formation water of reservoir B (1758 ppm), Sea water (43,000 ppm), 5 times diluted sea water (8747 ppm), 25 times diluted sea water (1749.2 ppm), 100 times diluted sea water (437.2 ppm). The core flooding experiments were performed by injecting several brines in tertiary mode, before reaching residual oil saturation (S_{or}). Formation brine was injected in secondary mode followed by injection of several brines of different salinities and compositions in tertiary mode. The experiments for rock samples from reservoir A were performed at 120^{o}C while for reservoir B samples; the experiments were performed at 70^{o}C. In both core flooding experiments, higher oil recovery was obtained on diluting the brines. While, a limit in the dilution was observed in different core plugs where on further diluting the sea water, no more oil recovery was obtained. They also performed a geochemical study by using PHREEQC software. They reported that the change of the brine salinities due to calcite dissolution is minor and may not improve oil recovery during

core flooding. They concluded that low salinity brines alter the rock wettability toward more water wet, while calcite dissolution cannot be the dominant mechanism of IOR by low salinity flooding since some of the injected brines that cannot dissolve calcite resulted in improvement of the oil recovery, and some other brine that dissolved calcite did not show any extra oil production.

Yousef et al. [62]–[65] measured fluid/fluid and fluid/rock interactions through interfacial tension measurements, contact angle measurements, NMR and surface charge measurements on carbonate reservoir core plugs. The rock was composed of 80 percent calcite, 13 percent dolomite and less than one percent quartz. Different salinity brines with formation water (213Kppm), sea water (57Kppm) and other diluted versions of sea water 2 times (2SW), 10 times (10SW), 20 times (20SW) and 100 times (100SW) diluted sea water were used in the experiments. Live oil was used in the study with Acid Number of 0.25mg KOH/g. They observed that as the salinity increases the IFT also increases. However, the effect of further dilution of sea water on IFT was negligible and this implies that diluting sea water primarily affects rock/brine interaction. The contact angle with connate water was measured to be about 90° while for twice-diluted seawater the measurements were about 80 degrees for carbonate brine/oil/rock system. The authors report a significant alteration in wettability with the 10SW with a measured contact angle of ~69°. The measurements with the other two brines such as 20SW and 100SW, showed no significant change in rock wettability toward the water-wet state.

The significant wettability alteration was observed with 2SW and 10SW. Their study also showed a change in the surface charges toward more negative in response of treating rock with diluted versions of sea water as measured by zeta potential. They also observed

anhydrite dissolution upon injection of diluted sea water that could supply additional SO_4^{2-} ions that are usually considered as one of the PDIs.

They concluded that calcite dissolution, caused by injection of low salinity brines, improves the connectivity between micropores and macropores and alters the rock wettability. This leads to improvement of oil recovery by LSF by improving the sweep efficiency. They proposed wettability alteration is the key mechanism for improved oil recovery and it can be achieved by manipulating the ionic composition of the field injection brine.

2.3 Effect of Rock Composition on Wettability Alteration

Mahani et al. [33] investigated the effect of synthetic brines on two carbonate minerals (calcite and dolomite) through contact angle and zeta potential (ζ) measurements. They used four brines. Formation water (FW~180Kppm), Sea Water (SW~43Kppm), 25 times diluted sea water (25dSW~1751ppm) and 25 times diluted equilibrated sea water to prevent calcite dissolution upon interaction with calcite (25dSW~1759ppm). Live oil was used in the study with acid number of 0.52 mgKOH/g. The experiments were conducted at 25°C. The ζ measurements were carried out in two batches. First, the experiments of calcite particles with various brine salinities and pH range were conducted, and then ζ measurements of oil with various brines were conducted. They observed that the ζ of SW and dSW were negative with values of -6mV and -14mV, respectively at pH of 6.6 except for formation water which had a zeta potential of +5.2 at pH of 6.6. The ζ of calcite particles in various brines increased when the pH increased. This is attributed to a higher positive charge at higher pH on calcite surface. For dolomite, the particles in formation water and sea water had positive charge throughout the pH range of 5.8-9.4. In both

minerals (calcite/dolomite), the increased dilution of sea water increased the iso-electric point (IEP). They concluded that dolomite rock reacts different as compared to limestone and exhibits more positive charge at the surface. From the oil/brine ζ measurements, they inferred that the charges at the oil/brine interface became more negative with decreasing brine salinity. Oil in formation water had a slightly negative ζ. The ζ in sea water was more negative (around −12 mV) and decreased further in 25 times diluted sea water (from −25 to −17 mV for $6 < pH < 10.5$). For SW and 25dSW, the zeta potential tended to become less negative by lowering pH below 7 and, at around 3−4 pH, the zeta potential reached close to IEP. The contact angle measurements were also in line with the ζ measurements with decrease of contact angle was observed with increasing dilution for limestone. The contact angle of aged dolomite decreased when FW injected after SW, but the injection of 25dSW immediately after FW did not change the contact angle of aged dolomite mineral. They explained this as a result of the adhesive forces between dolomite and oil and surface charge response of the mineral. In the other experiments, they controlled the mineral dissolution by conducting the experiments with both enhanced and prevented mineral dissolution. They concluded that sea water and diluted sea water cause wettability alteration with or without the presence of calcite dissolution. Calcite dissolution cannot be the main mechanism of improved oil recovery. Under the same conditions, the magnitude of the low salinity flooding effect was smaller for dolomite than calcite.

Romanuka et al. [66] observed the impact of low salinity in carbonates (chalk, limestone and dolomite) through spontaneous imbibition experiments. They used three crude oils: Oil A with AN of 0.920 mgKOH/g, Oil B with AN 0.42 mgKOH/g and Oil C with AN 0.070 mgKOH/g. Apart from that, large number of core samples and brine samples were

used in their study. The core samples include chalk from Stevns Klint outcrop, limestone (major component: calcite, minor component: dolomite, quartz) and dolomite plugs. Further, they used four formation water samples, synthetic sea water, aquifer water and several modified brines. The spontaneous imbibition tests were conducted at elevated temperatures of 60, 70 and 85^{o}C. The chalk formation showed highest oil recovery with the highest SO_4^{2+} concentration but not with the lowest ionic strength. For the limestone plugs, they observed that, lowering the ionic strength increased the oil recovery. However, removal of NaCl had no effect on one of the limestone rock samples. For the dolomite rock, wettability alteration occurred upon lowering the ionic strength. Incremental oil recovery due to wettability alteration was observed in the absence of significant anhydrite dissolution.

Ferno et al.[67] investigated the impact of increased [SO_4^{2-}] in the imbibing fluid through spontaneous imbibition (SI) at various wettability conditions at 130^{o}C. Crude oil was aged in three different chalk outcrops Stevns, Rordal and Niobrara. Only one type of rock that is Stevns chalk showed incremental oil recovery with increased [SO_4^{2-}] in the imbibing water, while the other two chalks did not result in additional oil recovery by increasing [SO_4^{2-}] in the brine. For Niobrara Chalk at 130^{o}C, Amott water indices showed increased in water-wetness, before and after SI. Rordal and Stevns chalks did not modify wetting preference after SI at high temperature and kept less water wet SI characteristics at normal temperature, in any case if SO_4^{2-} was added or not. Increased oil recovery was observed in Rordal core plugs by SI at high temperature, but the wetting condition was not changed. They concluded that the contribution of SO_4^{2-} on SI in chalk is dependent on the chalk mineralogy and the wetting characteristic of the rock.

2.4 Effect of Brine Composition on Wettability Alteration

Al-Hashim et al. [68] investigated the effect of smart water by core flooding tests through sequential dilution and injection of formulated brines. Core plugs from Middle East carbonate reservoir were used for core flooding and zeta potential measurements. The XRD analysis showed the core samples were mainly 80% calcite and 18% dolomite with small percentage of anhydrite. 16 brines were prepared by adjusting the concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- of 50% diluted sea water. Connate water (213,000 ppm), sea water (57,000 ppm), twice diluted and 10 times diluted brines were also included. Zeta potential (ζ) measurements were first conducted to select optimal brines out of 16 formulated brines using analysis of variance (ANOVA). Crude oil (dead oil) with base number of 0.15 mgKOH/g from Middle East carbonate reservoir was used in this study. The core flooding experiments were conducted at 100°C. Three core flooding experiments with different dilution sequences of injected brines were performed. It was concluded that the increase in oil recovery is dependent on the sequence of injection of sea water and not necessarily on the sequential dilution of sea water.

Murtdha and Jagannathan [69] investigated the effect of composition of brines on carbonate wettability. They used calcite samples in their study. The tests were conducted at 63°C. A total of 27 experiments were conducted to measure interfacial tension (IFT) and contact angle by utilizing Taguchi technique. Overall six salts were used to make brines of different salinity. They are $MgSO_4$, $CaSO_4$, Na_2SO_4, NaCl, $CaCl_2$ and $MgCl_2$. The salinity ranged from 14Kppm to 333Kppm. They observed that the interfacial tension between oil and water increased as the brine salinity increased. Test runs with similar brine salinity but different composition showed different wettability. The highest brine salinity showed the

highest contact angle while the lowest brine salinity did not show the lowest contact angle. After performing analysis of variance (ANOVA) and experimental verification, they found out that the lowest contact angle was 28.9^{o} with brine salinity of 157,207 ppm which is relatively high. They also concluded that sodium chloride and calcium chloride are major salts that alter the calcite wettability.

Fathi et al. [70] investigated the effect of smart water flooding on chalk formation by using spontaneous imbibition test and chromatograph wettability test. They studied the effect of salinity, monovalent and divalent ions. The formation brine had a salinity of 65000ppm with no sulfate concentration.

For monovalent ions, they varied NaCl concentration (0, 1 and 4 times sea water(SW) salinity) while keeping [Ca^{2+}], [Mg^{2+}] and [SO_4^{2-}] constant and equal to concentration of these ions present in SW. The spontaneous imbibition experiments were performed at 100, 110 and 120^{o}C. Spontaneous imbibition tests indicated that the oil recovery increased as NaCl concentration decreased in SW. Oil recovery also increased at high temperature. Oil recovery decreased when diluting SW from 33000ppm to 10,000ppm and 20,000ppm.

For divalent ions, they varied the concentration of Ca^{2+} and SO_4^{2-}. In their study, they used two initial wetting conditions. Oil A with AN = 2 mgKOH/g and Oil B with AN = 0.5 mgKOH/g. The cores were saturated with Oil A at higher temperature 100-120^{o}C while for lower temperature 70-90^{o}C, the cores were saturated with Oil B. For oil B, the spontaneous imbibition experiments were performed with SW, sea water without NaCl(SW0NaCl) and SW without NaCl but sulfate concentration spiked to 4 times (SW0NaCl-4SO_4^{2-}).

Oil recovery increased as they changed the concentration from SW to SW0NaCl to (SW0NaCl-4SO_4^{2-}) for both temperatures 70^{o}C and 90^{o}C but the recovery was relatively

high in the case of high temperature. For oil A, the spontaneous imbibition experiments were performed with sea water without NaCl(SW0NaCl), SW without NaCl but sulfate concentration spiked to 4 times (SW0NaCl-4SO_4^{2-}) and SW without NaCl but calcium concentration spiked to 4 times (SW0NaCl-4Ca^{2+}). At 100^{o}C, oil recovery increased as the concentration changed from SW0NaCl to SW0NaCl-4SO_4^{2-} but no significant oil recovery was obtained with SW0NaCl-4Ca^{2+}. At 120^{o}C, the response was the same but only an increase of 4% in oil recovery was observed from SW0NaCl-4Ca^{2+}.

They also measured the water wet fraction (WI) for different imbibing fluids where WI = 0 indicates the complete oil wet while WI = 1 indicates the complete water rock. The water wet fraction of the core after imbibing the core with formation water at 90^{o}C was WI = 0.44 (preferentially oil wet). The results from different imbibing fluids showed that as the water wet fraction of the rock surfaces increased from 0.44 to 0.6, the oil recovery increased from 17% to 62% of OOIP.

Gupta and Mohanty [71] investigated the wettability alterations in fractured carbonate reservoirs. They studied the effect of salinity, electrolyte concentration, surfactant concentration and temperature on wettability alteration. They performed wettability and spontaneous imbibition tests. The spontaneous imbibition tests were conducted at 90^{o}C. The study concludes that, as temperature increases, contact angle for a brine/oil/calcite system decreases toward more water-wet values. It is found that the wettability can be altered by the addition of divalent ions at high temperature (90^{o}C and above). They found sulfate ions to alter the wettability more when the other two ions such as Ca^{2+} and Mg^{2+} are present in the brine than when they are not present. Magnesium ion alone cannot alter wettability unless sulfate ions are also present in the brine. Calcium ions alone can change

the wettability but are needed in greater concentration (five times the base value) to affect the change. Calcium ions can change the wettability toward water wet even more in the presence of sulfate ions.

Strand et al. [72] investigated the effect of brine composition by analyzing brine/rock interaction on limestone cores from Middle East reservoir through spontaneous imbibition tests and core flooding experiments. The spontaneous imbibition tests were conducted at 120^{o}C with initial formation brine salinity of 180Kppm. The core flooding experiments were conducted at different temperatures ranged from 20-130^{o}C and the effluent was analyzed for Ca^{2+}, Mg^{2+} and SO_4^{2-}. They analyzed that at low temperatures 20^{o}C and 70^{o}C, Ca^{2+} and Mg^{2+} behaved similarly toward the carbonate surface but when they increased temperature to 100^{o}C and 130^{o}C, the behavior of Mg^{2+} ion became prominent than that of Ca^{2+}. By analyzing the effluent of the experiments, they observed that there was no increase in Ca^{2+} concentration using limestone reservoir cores. This is evident that the limestone surface is less reactive than chalk. Mg^{2+} substituted Ca^{2+} when sea water flooded the limestone very slowly. The concentration of SO_4^{2-} was unchanged for the different temperatures values. In case of Ca^{2+}, the concentration was increased when the temperature was raised above 100^{o}C. Furthermore, the Mg^{2+} concentration decreased at 130^{o}C. When mixing formation brine with high sulfate concentration, they observed that spontaneous imbibiton of the brine is restricted by precipitation of $CaSO_4$ in the pore system.

Austad et al. [23], [23], [23], [73], [74] performed an extensive study of smart water on chalk formation through spontaneous imbibition experiments. They concluded that sea water could act as wettability modifier at high temperature due to active ions Ca^{2+}, SO_4^{2-} and Mg^{2+}. They observed that at a given temperature, the adsorption of SO_4^{2-} increased as

Ca^{2+} increased. He also pointed out that for wettability modification; the imbibing water must contain either Ca^{2+} and SO_4^{2-} or Mg^{2+} and SO_4^{2-} ions. They also indicated that concentration ratio [SO_4^{2-} /Ca^{2+}] in the injected water to be an important parameter. This was determined from the depletion of SO_4^{2-} ion in the effluent from the core flooding chalk cores with sea water that has a ratio of [SO_4^{2-}] ~ 2[Ca^{2+}]. In another study, they observed that the wetting index decreases as Acid Number (AN) increase.

Bagci et al. [75] investigated the effect of brine composition on oil recovery by water flooding using limestone cores. They used NaCl, $CaCl_2$, KCl and binary combination of them. They varied the salinity of each salt and analyzed the effect of each salt separately through core flooding. A total of 15 water flooding experiments were conducted in their study. All experiments were conducted at 50^{o}C. The highest oil recovery of 38 % OOIP was observed with 2 wt.% KCl. Incremental oil recoveries were observed by decreasing injected brine salinity. For 10 wt.% KCl, no oil production was obtained due to core plugging. They concluded that modifying the composition of injected brine can offer an economically feasible way to increase oil production.

Moshood [76] studied rock/oil/brine interaction by using zeta potential and surface adsorption techniques. He used precipitated calcium carbonate (PCC) with purity more than 99% and limestone rock that was mainly comprised of dolomite~73% and calcite~25% with small amount of anhydrite~2%. 16 different brines were prepared by adjusting the concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- ions from the composition of 50% diluted sea water. Sea water (salinity~57,600 ppm), and 50% diluted sea water brines were also included. Reservoir crude oil was used in this study. Adsorption test was carried out by analyzing the change in concentrations of ions before and after treatment of respective

brines with rock. All adsorption tests were conducted at temperatures of 25ºC and 90ºC. Ionic concentrations of brines were determined by using ICP-OES. All experiments were conducted for both unaged and aged rock with oil. He concluded that PDIs' interaction with the rock surface is dependent on the rock type, composition of brine, reservoir temperature and presence of crude oil. Calcium, magnesium, and sulfate ions will adsorb onto PCC from brine, and the magnitude of adsorption is directly proportional to the concentration of these ions in brine. Adsorption of calcium and magnesium ions onto PCC increased with temperature, and substitution of calcium ion on the PCC crystal lattice by magnesium ion increased significantly with temperature. Temperature increase altered the adsorption interactions of ions with limestone, by mostly the substitution reaction of magnesium ion, and the decrease in sulfate desorption from the limestone. Limestone is negatively charged in seawater at pH range of 7.4 to 7.5. This surface charge was found to vary with different brine compositions, and the presence of crude oil generally decreased the zeta potential of limestone in seawater at 25°C. Furthermore, increase of temperature reduced the surface charge of PCC and limestone in brine.

Jabbar et al. [77] investigated the wettability alteration of calcite crystal and carbonates outcrop rock surface aged in model oils of total acid number of 2 and then treated with different brines. Model oils were prepared by mixing toluene with short chain (Heptanoic acid) and long chain (Stearic acid) carboxylic acids and the investigated brines included range of salinity and the effect of individual ions such as Ca^{2+}, Mg^{2+} and SO_4^{2-}. The results showed that the long chain fatty acid (stearic acid) strongly adsorbs onto the calcite surface from the oil phase compared to the short chain (heptanoic acid) as confirmed by the measured contact angles. Twice dilution of Arabian Gulf seawater has been found to be a

less efficient EOR fluid for wettability alteration as compared to undiluted Arabian Gulf seawater. This was confirmed by the changes in the measured contact angles toward more water-wet for aged calcite in heptanoic acid model oil, aged calcite in stearic acid model oil and aged carbonate in stearic acid model oil systems. Sulfate ion had the largest effect on wettability in the presence of magnesium and calcium ions. The presence of Mg^{2+} ions has inconsiderable effect on wettability of calcite as compared to the reference measured DIW. However, Mg^{2+} has shown as a potential ion towards the carbonate surface and the surface is altered towards more water-wet with increasing the concentration of Mg^{2+} ion.

2.5 Wettability Alteration Effect through Zeta Potential Measurements

Kasha et al. [32] studied the effects of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions on the zeta potential (ζ) of calcite, middle east carbonate (MEC) rock and dolomite particles aged with stearic acid. They found that in deionized water, the native and aged calcite particles have negative ζ while the dolomite particles have positive ζ. Increasing the higher concentration of divalent Ca^{2+} and Mg^{2+} ions increased the original positive ζ of the aged dolomite particles and altered the zeta potential of the aged calcite from negative to positive. The SO_4^{2-} ions caused the original negative ζ of the aged calcite to be more negative and altered the ζ of the aged dolomite from positive to negative. ζ measurements showed the affinity of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions is affected by the presence of other potential determining ions. The presence of Mg^{2+} ions significantly affects the ability of SO_4^{2-} ions to modify the original surface charges of aged calcite and aged dolomite while the presence of Ca^{2+} ions has less significant effect on the negative surface charges developed by SO_4^{2-} ions. Arabian Gulf Seawater adds more negative charges to carbonate surfaces compared to diluted seawater. When diluted Arabian Gulf seawater was used after primary conditioning of the carbonate

particles by original Arabian Gulf seawater, the magnitude of negative charges in the calcite, MEC and the positive charges in the dolomite has increased compared to when the diluted seawater is directly used. By such sequential conditioning, adsorbed carboxylic materials are believed to be released by the induced dissolution of the carbonates minerals rather than ions exchange/adsorption.

Awolayo et al. [78] investigated the effect of smart water on Middle East carbonate core plugs. They used formation water (FB) and synthetic sea water (SSB) as a baseline. They varied the sulfate concentration in SSB in a ratio of 0.5:1:2:4:8 where 0.5-times refer to SSB#0.5S similarly SSB#2S, SSB#4S, and SSB#8S. In their study, they performed core flooding experiments, zeta potential (ζ) and contact angle measurements. Reservoir dead oil collected from a carbonate reservoir with 37^{o}API at room temperature and 1.927cp viscosity at 158^{o}F was used in this study. Core flooding experiments were performed at temperature of 230^{o}F and the produced fluid was collected to quantify oil recovery and ionic concentration by ion chromatography. The average permeability and the porosity of the core plugs were 39.6 md and 25% respectively. XRD analysis showed the rock samples comprised of mainly calcite with little dolomite and quartz. ζ was measured by Zeta Electro Acoustic Spectrometer. The ζ and contact angle measurements were carried out at 60^{o}F and 203^{o}F, respectively. The ζ measurements showed all positive values for all brines used starting from +4.49 mV in FB at unadjusted pH of 7.33. The zeta potential decreased with increasing sulfate concentration in the synthetic brines except for 8 times sulfate concentration where zeta potential slightly increased. This is attributed to the precipitation of $CaSO_4$ at such high concentration of sulfate in SSB. The pH increased with increasing sulfate concentration except for 2 times sulfate concentration in brine. The contact angle

measurements were also in line with the zeta potential measurements with reducing brine salinity reduced the contact angle. The core flooding experiments showed oil recovery of 66.6% with FW, followed by 2.89% incremental recovery with SSB#2S, followed by 5.71% with SSB#4S and 1.11% with SSB#8S. They concluded that, additional oil recovery was observed by altering the brine ionic composition, especially sulfate. A direct relation seems to exist between increased SO_4^{2-} concentration and zeta potential where increasing the sulfate concentration in the SSB reduces the magnitude of zeta potential.

Taqvi et al. [79] studied the zeta potential of aqueous limestone suspension with addition of asphaltene solutions. Three different concentrations of asphaltene solutions with a mixture of n-heptane insoluble asphaltene and toluene were used in this study. For all concentrations, the zeta potential (ζ) decreased exponentially by the addition of the asphaltenic solutions. Highest negative ζ value was observed with the solution of highest asphaltene content. Alternatively, lowest negative zeta potential value was observed with the solution of least asphaltene content.

Chen et al. [80] studied the effect of salinity on limestone through zeta potential. Limestone core was collected from an oil reservoir in Xinjiang, China. Synthetic formation brine was formulated with salinity equal to 223 Kppm. All zeta potential (ζ) measurements were conducted at 25^{o}C temperature and the pH values of the solutions were maintained at 8. Phase Analysis Light Scattering (PALS) technique was applied to measure ζ. Asphaltene solutions with n-hexane was used to make limestone oil wet. Four different types of limestone rocks were used in this study with calcite being the major component. Effect of limestone particles with three different salts such as $CaCl_2$, $MgCl_2$ and NaCl were investigated using zeta potential measurements separately with increasing concentration of

each salt solutions. Zeta potential increased with increasing concentration from 0.0001 wt.% to 1 wt.% of each brine. However, all zeta potential values were negative for this range. NaCl and $CaCl_2$ showed the lowest and highest zeta potential values, respectively for all concentration range (0.0001 wt.% to 1 wt.%). When the concentrations increased to 10 wt.%, zeta potential of $CaCl_2$ and $MgCl_2$ shifted toward positive after 3wt.% and 6wt.% respectively. While for Na^+, ζ was still negative. After analyzing different carbonate rock samples, they concluded that increasing the calcite content results in the increase of ζ value. The adsorption of oil polar fractions and naphthenic acid is favorable to the increase of the ζ, but the effect of salinity on the ζ is more remarkable than that of the adsorption.

Yousef et al. [34], [62]–[65], [81], [82] conducted the zeta potential measurements of a Middle East carbonate rock suspension on diluted versions of Arabian Gulf Sea water. All experiments were performed at two different temperatures 40ºC and 60ºC. Zeta potential measurements showed more negative values with reduction of ionic strength of sea water. At 40ºC zeta potentials were negative at 50% diluted AGSW and as the salinity decreased the absolute value of negative charges increased. Increasing the temperature to 60ºC increased the magnitude of the negative charge, which was attributed to adsorption of SO_4^{2-} with co-adsorption of Ca^{2+} on carbonate surface. Mg^{2+} ions will replace the Ca^{2+} ions from the rock surface and the increased solubility of Ca^{2+} ions which will force Ca^{2+} to leave the carbonate surface that will results in more negative charges at the surface.

Alotaibi et al. [25] investigated the zeta potential (ζ) measurements on limestone and dolomite rock of the Middle East reservoirs, in different synthetic brines. The experiments were conducted at two different temperatures 25ºC and 50ºC. At 25ºC and pH equal to 7, they found that zeta potential for the limestone particle is positive in Arabian Gulf sea water

which was due to the weak electrostatic repulsion caused by compression of the electric double layer (EDL). The ζ of aquifer water (5436 ppm) became more negative as the aquifer water was twice diluted. In aquifer water, ζ had an ascending trend with pH as increasing the pH improved the zeta potential. They found that increasing the temperature to 50^{o}C results in more negative charges for the limestone particles suspended in aquifer water. They concluded that low salinity water creates more negative charges on rock particles (limestone and dolomite) due to the expansion of EDL thickness and increasing the temperature will significantly decrease the zeta potential. No significant effect on the surface charge was observed with monovalent ion (Na^{+}).

Gomari et al. [83] investigated the impact of Mg^{2+}, SO_4^{2-} and HCO_3^{-} on altering the wettability of carbonate rock. They conducted contact angle measurements and zeta potential (ζ) measurements on calcite with different brines. Stearic Acid and Phenoloctadecanoic acid (PODA) were used to alter the wettability of calcite toward more oil wet. The ζ measurements were carried out to check the influence of Mg^{2+}, SO_4^{2-} and HCO^{3-} ions. All experiments were conducted at temperature of 25^{o}C. As the concentration of Mg^{2+} ion increased, the ζ shifted toward positive while the concentration of SO_4^{2-} and HCO^{3-} ions reduced the ζ toward more negative value which is attributed to the displacement of carboxyl charges from the calcite surface. The contact angle measurements showed that increasing Mg^{2+} ion concentration from 0.02M to 0.06M reduced the contact angle from 74^{o} to 28^{o} and 15^{o} respectively. This is attributed to the replacement of Ca^{2+} ion by Mg^{2+} and promoting the carboxyl to leave the calcite surface, resulting in more water wet surface. They concluded that Mg^{2+} converted the calcite surface to more water wet than SO_4^{2+} ion. Both ions have affinity to adsorb on the calcite surface.

Rodriguez and Araujo [84] observed temperature and pressure effect on zeta potential (ζ) of three mineral; Calcite, Kaolinite and quartz. Electrolyte concentration was varied in the range from 0.0001 to 0.1 M in the pH range from 2 to 9. Zeta Meter 3.0 with in-house modification for pressure control was used for determining zeta potential. For all minerals, the ζ decreased with temperature at an order of −2.3 mV/◦C, −0.96 mV/◦C and −2.1 mV/◦C for quartz, kaolinite, and calcite respectively, for pressure below 45 psig. A systematic increase in ζ values with pressure was observed for quartz at all pH values, while a monotonic decreasing trend was observed for the kaolinite. The calcite response is variable with pressure. A decreasing trend was observed for pressures less than 45 psig.

Zhang and Austad [30] investigated the effect of Ca^{2+} and SO_4^{2-} ions through zeta potential (ζ) measurements. The experiments were conducted at 25^{o}C. It was found that the increase in concentration of Ca^{2+} shifted the zeta potential towards more positive and the positive value of zeta potential increased linearly with increasing the concentration of Ca^{2+}. While, SO_4^{2-} shifted zeta potential to negative and as the concentration increased, the zeta potential decreased linearly. To measure the relative effect of Ca^{2+} and SO_4^{2-}, they kept the concentration of one ion fixed while varied the concentration of the other ions and measured the zeta potential (ζ) at different concentration ratio. They observed that ζ is close to zero when the ratio between [SO_4^{2-}]and [Ca^{2+}] ions was about 1 and it became positive when [Ca^{2+}] was in excess of [SO_4^{2-}] and negative when [SO_4^{2-}] exceeded [Ca^{2+}]. They concluded that the injected seawater that contains Ca^{2+} and SO_4^{2-} can increase the water wetness of chalk and when these ions are contained, the ζ will be dictated by the concentration ratio of SO_4^{2-} /Ca^{2+}. From spontaneous imbibition tests, it was found that, at a given temperature, the oil recovery increased as the ratio of SO_4^{2-} and Ca^{2+} increased.

2.6 Wettability Alteration Effect through Atomic Force Microscopy

Abdallah and Gmira [85] studied calcite dissolution after treatment with different brines and monitored the aging of calcite in crude oil at 60 °C by using Atomic force Microscopy (AFM). Then, they investigated the surface interaction of potential determining ions (Ca^{2+}, Mg^{2+}, and SO_4^{2-}) by using synthetic brines of different composition with aged calcite rock. Dead crude oil of 0.11 mg KOH/g acid number and 6.40 weight percent of asphaltenes with synthetic sea water SWME (1.15 mol/L) similar to Arabian Gulf sea water was used in this study. Ionic strength of synthetic brines was kept constant at 0.57 mol/L.

Calcite surface treated with synthetic brine was analyzed by AFM for topographical change. They observed that when the calcite surface, followed by aging in crude oil, is treated with 200 Kppm NaCl, a complex surface morphology is observed with precipitation of different chemical species. At the calcite surface, a non-uniform adsorption of crude oil species was observed. When 50% diluted sea water (termed as SWME*) was used, mound shape features as well as flat layered structures observed on the surface. Without magnesium ions in the brine, no mound structures were visible. With Magnesium ion, polishing marks disappeared and mound shape features appeared, which depicts the adsorption of magnesium ion at the surface.

As the sulfate content increased in the synthetic brine, they observed the presence of anhydrite surfaces with atomically flat terraces bounded by cleavage steps. Moreover, 4 times sulfate concentration in the SWME* resulted in most effective surface wettability alteration. The increase in the Ca^{2+} concentration increased the calcite dissolution rate with typical rhombohedra shapes observed on the calcite surface.

Karoussi and Hamouda [86] studied the effect of Mg^{2+} and SO_4^{2-} on wettability alteration of modified calcite surface to oil-wet by stearic acid (SA) using contact angle and atomic force microscopy technique (AFM). The individual effect of magnesium and sulfate ions on desorbing carboxylic groups was not fully distinguished using AFM topology images. However, the AFM results correlated well with contact angle measurements for treated calcite surface with Mg^{2+} or SO_4^{2-}. Adhesion force measurements were found to be in agreement with the contact angle measurements which showed that magnesium ions were able to alter the wettability of the modified calcite towards more water wet compared to sulfate ions. They concluded that the presence of the magnesium ions increases the water wetness of modified calcite.

In summary, it is observed from aforementioned studies that the reservoir rock wettability is influenced by many parameters including injected brine and rock composition, reservoir temperature and acid number of oil. However, the only adjustable parameter to induce smart water effect in the reservoir is the brine composition. Several studies have shown wettability alteration using high salinity brines with adjusted ionic concentrations. Therefore, it can be stated that smart water is not only brine of low salinity and low ionic strength, but it could be higher salinity brine with specific ionic concentration. It is a general trend that the increase of positive ions or cations increase the positive charge on the rock surface while the increase of negative ions or anions increase the negative surface charge. It is also observed that the adsorption of polar oil components on the rock surface increase the negative charge. As a result of alteration of rock surface charges due to injection of smart water, the carboxylic oil which is adsorbed on the carbonate surface

desorbs, and consequently rock wettability is altered to less oil wet and more water wet condition.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Rock Samples

In this study, two different limestone rock samples are used, Calcite-Iceland spar crystals from Chihuahua, Mexico (Ward's Natural Science) and carbonate rock samples collected from Arab-D carbonate outcrop (provided by Schlumberger Middle East).

Rock samples were crushed to a particle size between 10 nm to 30 nm to meet the requirements of the zeta potential instrument (Brookhaven ZETAPALS) used in this study. In order to make very small particles, both rock samples were crushed and grinded through two different instruments supplied by RETSCH. Rock samples were first crushed by a Jaw Crusher to produce particles size within the acceptable range of the Ball Mill, which could produce a particle size up to 2 μm. The produced powder from the Ball Mill was transferred into a clean glass bottle to avoid contamination followed by mineralogy analysis using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) as shown in Table 2, Figure 1 and Figure 2. Calcite rock shows pure calcium carbonate while carbonate outcrop contains calcium carbonate with small percentage of silica.

Table 2: Mineralogical and elemental composition of calcite and carbonate rock particles through XRD and XRF analysis.

Samples	XRD analysis	XRF analysis	
Calcite	Calcite, $CaCO_3$ ~ 98% Dolomite, $CaMg(CO_3)_2$ ~ 1% Albite, $NaAlSi_3O_8$ ~1% Quartz, SiO_2 ~ Traces (< 1%)	Element Calcium Impurities Sulphur Magnesium Manganese Silver	Wt.% 99.085 0.111 0.128 0.107 0.174
Outcrop carbonate rock	Calcite, $CaCO_3$ ~ 95% Quartz, SiO_2 ~ 4% Dolomite, $CaMg(CO_3)_2$ ~ 1%	Element Calcium Silicon Impurities Iron Aluminum Phosphorus Sulphur	Wt.% 95.414 1.895 0.926 0.703 0.193 0.119

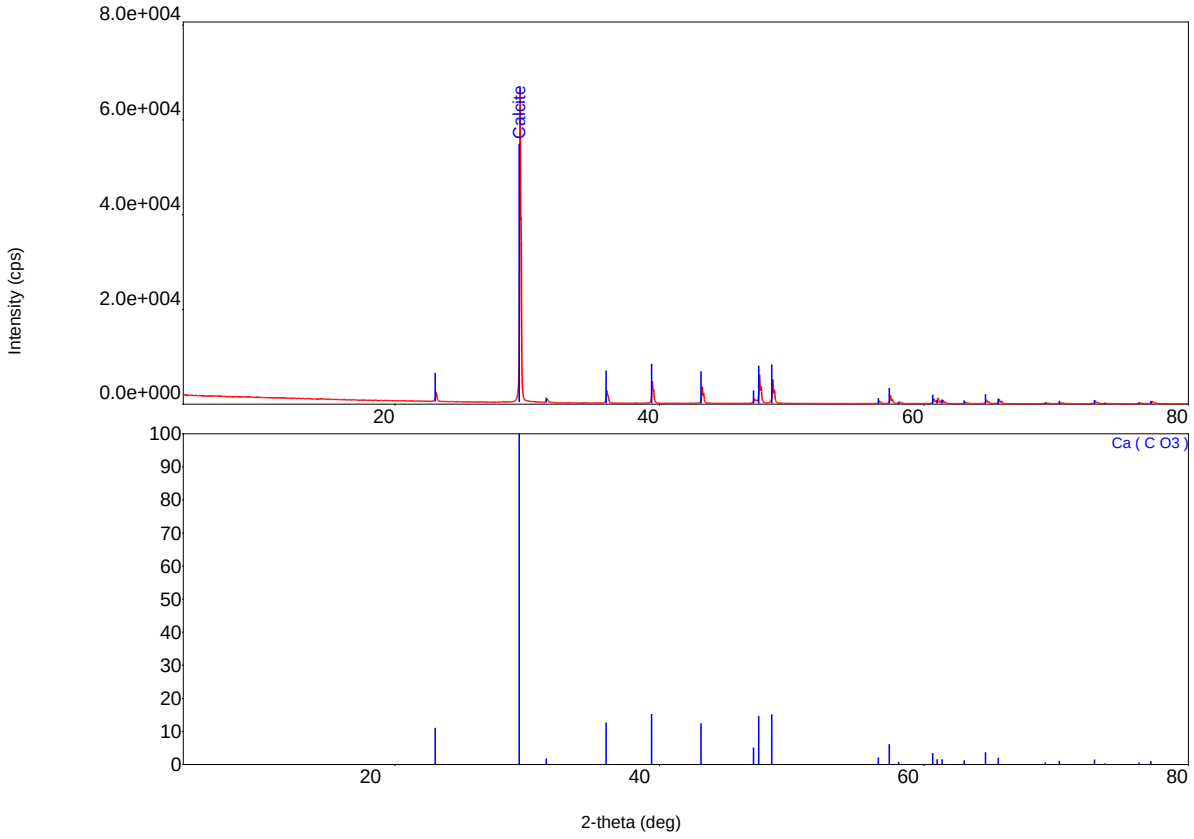

Figure 1: XRD spectra of calcite rock powder.

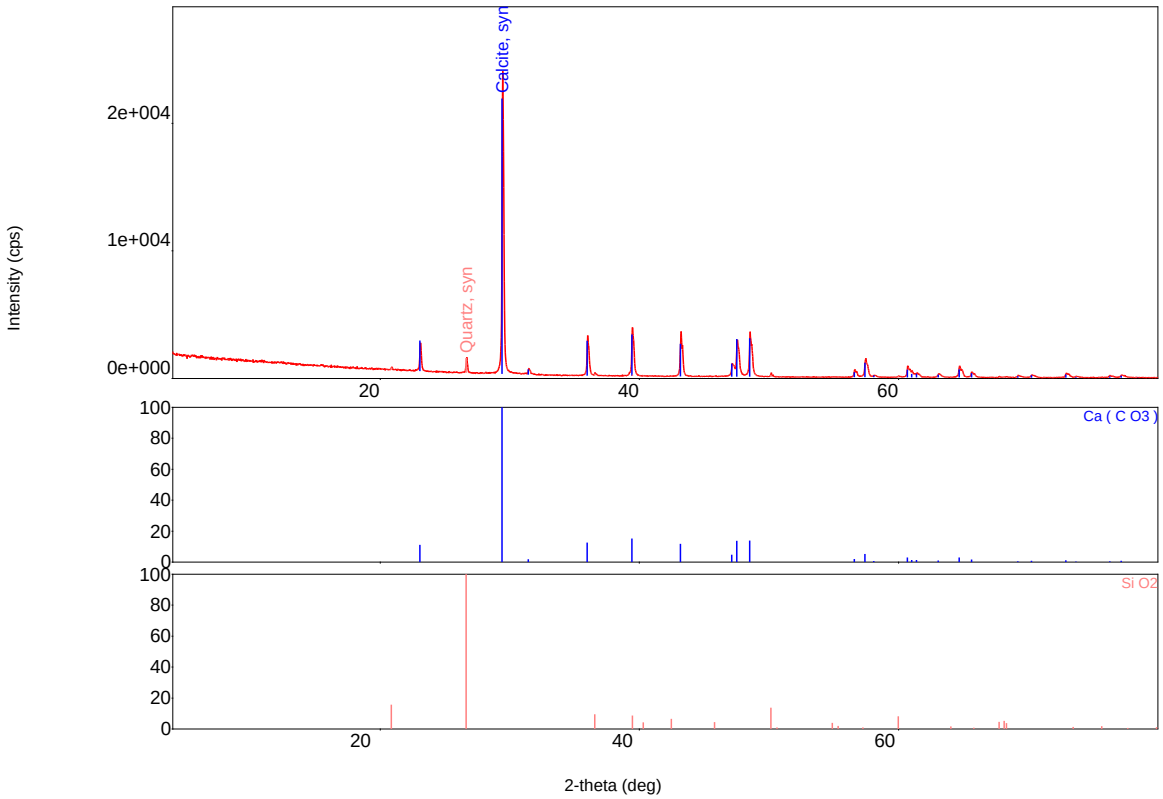

Figure 2: XRD spectra of carbonate outcrop powder.

3.1.2 Brines

Table 3 shows seven different brines synthesized for the current study to investigate the impact of each anion on the rock surface characteristics. The brines were prepared using laboratory grade salts and de-ionized water (resistivity of 18.2 MΩ·cm at 25^{o}C) and were conditioned using a magnetic stirrer with moderate speed (40 rpm) for 1 hour at room temperature. After conditioning, all brines were filtered through 0.45 µm filter paper by using vacuum pump, flask and a glass funnel. After filtration, dissolved gases were removed from brines using a vacuum pump. High purity salts such as NaCl, $MgCl_2.6H_2O$ purchased from Loba-Chemie, $NaHCO_3$, NaI and NaBr purchased from Sigma-Aldrich, $CaCl_2.2H_2O$ purchased from Scharlau, Na_2SO_4 purchased from Techno-Pharmchem were

used in this study. De-ionized (DI) water was produced by Barnstead Ultrapure Water System manufactured by Thermo Scientific. DI water was used for cleaning the instruments and for some zeta potential measurements. Table 3 shows the concentration of salts and ions in the prepared brines.

Table 3: Different brines used in the study.

	Brines	Salts/Ions			Total Salinity (ppm)	Ionic Strength (M)
Low Salinity brines	**DyW1**	NaCl			5000	0.086
	DyW2	NaBr			5000	0.049
	DyW3	NaI			5000	0.033
High Salinity brines	**SW (Sea Water)**	Na^+ 18,043 ppm	Ca^{2+} 652 ppm	Mg^{2+} 2,159 ppm	57,365	1.15
		Cl^- 31,890 ppm	SO_4^{2-} 4,450 ppm	HCO_3^- 173 ppm		
	DyW4 (SW0.5NaCl)	Sea Water + 0.5 % NaCl				
	DyW5 (SW0.5NaBr)	Sea Water + 0.5 % NaBr			62,365	1.23
	DyW6 (SW0.5NaI)	Sea Water + 0.5 % NaI			62,365	1.19

3.1.3 Model Oils

Three model oils were used in this study with a combination of stearic acid ($CH_3(CH_2)_{16}COOH$) and/or asphaltene dissolved in toluene. Based on the principle that "like dissolve like", toluene is served as an aromatic solvent for asphaltene [92] and a non-polar organic solvent for stearic acid [93]. First model oil with stearic acid/toluene (termed as TS), prepared by adding 0.415 grams of stearic acid in 43.35 grams-toluene, which is equivalent to a total acid number (TAN) of 2 mg KOH/g. Second model oil with 0.35 wt% asphaltene in toluene (termed as TA), prepared by adding 0.02167 grams of asphaltene in 43.35 grams-toluene. Third model oil with stearic acid/asphaltene/toluene (termed as TSA), prepared by adding 0.415 grams of stearic acid and 0.02167 grams of asphaltene in 42.9 grams-toluene. The model oils were prepared from high purity materials purchased from Sigma-Aldrich (>98.5% and ~99.8% purity for stearic acid and toluene, respectively). Table 4 presents a summary of the model oil used in this study along with their compositions.

Table 4: Composition of model oil components.

	Model Oil (TS)	**Model Oil (TA)**	**Model Oil (TSA)**
Stearic acid	0.415 g	-	0.415 g
Asphaltene	-	0.02167 g	0.02167 g
Toluene	43.35 g	43.35 g	42.9 g
Final mixture	43.765 g	43.37167g	43.33667 g

3.2 Zeta Potential Measurements

3.2.1 Scope of work

All zeta potential (ζ) measurements were carried out using ZetaPALS instrument supplied by Brookhaven Instruments Corporation. ζ is measured by the electrophoretic mobility of a particle suspended in a solution. The instrument applies a technique of Electrophoretic light scattering (ELS) in which a beam of laser light is passed through the solution which is kept under an applied electric field. [94]. The charged particles of the solution move toward the positive or negative electrode due to applied electric field. The ZetaPALS instrument is an extension of the ELS (Electrophoretic light scattering) technique. It uses phase analysis light scattering techniques, which are much more sensitive than conventional ELS.

ELS measures the velocity of moving particles that scatter laser light. Particles dispersed in a liquid often have a charge on the surface. The instrument applies an electric field in the liquid by a palladium electrode, the particles that carry electric charges move toward positive or negative pole of the electrode. Analyzing the direction of movement indicates electric charge on the particle and analyzing the velocity of particle measures the mobility of the charged particle. The zeta potential is then calculated by the mobility and applied electric field [94] as shown in equations 1 and 2.

$$v_e = u_e * E \quad \text{..... (1)}$$

Where v_e is the measured electrophoretic velocity and E is the applied electric field while u_e is the required electrophoretic mobility to calculate zeta potential. By calculating the electrophoretic mobility of a particle, the zeta potential may then be determined using the Henry Equation.

$$u_e = \frac{2\,\varepsilon\,\zeta\ f(Ka)}{3\,\eta} \text{..... (2)}$$

Where ε is the dielectric constant, ζ is the zeta potential, f(Ka) is Henry's function, and η is the viscosity. Henry's function generally has value of either 1.5 (Smoluchowski's approximation) or 1.0 (Huckel's approximation). Smoluchwski's approximation considers particle size radius larger than the double layer thickness and Huckel's approximation considers the particle size radius smaller than the double layer thickness. In this study, zeta potential is determined by using Smoluchowski's approximation that is acceptable for aqueous media with moderate particle size. The double layer thickness is usually in few nanometers [92], [95]–[97], while our average particle sizes are 1.3 μm and 1.7 μm for calcite carbonate outcrop, respectively. Particle sizes were determined by DLS (Dynamic Light Scattering) technique using ZetaPALS instrument. Figure 3 presents a flowchart of zeta potential measurements made in this study.

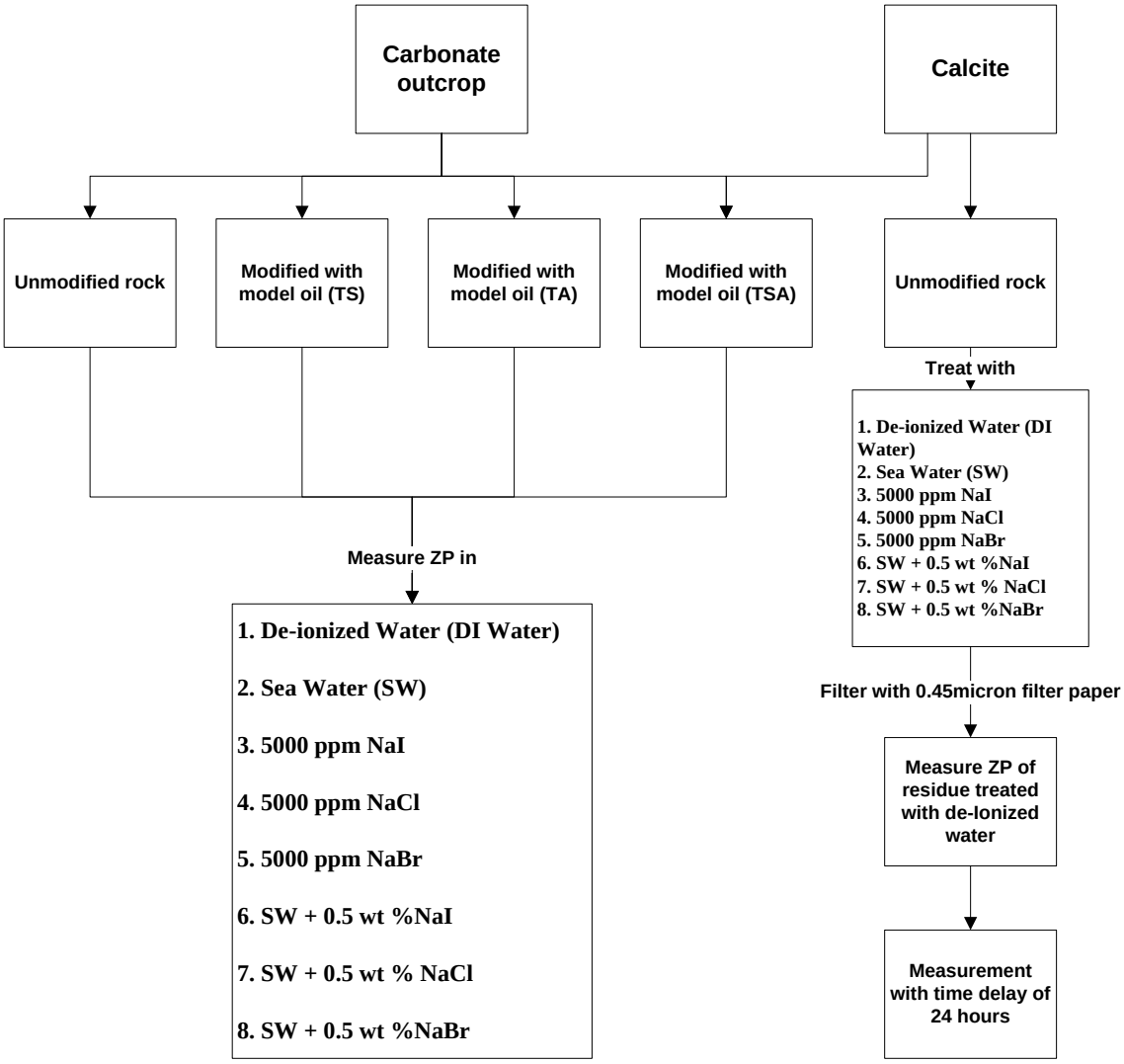

Figure 3: Flow chart of zeta potential measurements

3.2.2 Sample Preparation

For zeta potential measurement, a solid to liquid ratio should be chosen such that the result is independent of the concentration chosen [98]. Solid to liquid ratios used in the literature particularly for calcite particles were ranged between 0.04-1.00 wt% [25], [32], [33], [80]. In this study, a constant ratio of 0.50 wt%, which is recommended in the instrument manual [94] was used for all the zeta potential measurements. Therefore, a solution consists of 0.15 g of unmodified rock powders and 29.85 g of the respective brine were prepared for calcite

and carbonate outcrop for the case of unmodified rocks. Then, both solutions were conditioned in multi-wrist shaker at 40 rpm for 24 hours under room temperature. After conditioning, pH of both solutions were measured, it was observed that pH of low salinity brines (5,000 ppm NaCl, 5,000 ppm NaBr and 5,000 ppm NaI) were unstable and changing with time. After another 24 hours of incubating the suspension without shaking, pH was stable at constant values of pH were observed as shown in Table 5. Thus, a minimum of additional 24 hours was found to be reasonable to get stable pH values after 24 hours conditioning. For all measurements, solutions were allowed to reach equilibrium for 24 hours after conditioning before taking ζ measurements.

Table 5: pH values of calcite treated with different salt solutions with time intervals

Calcite suspended in	pH values		
	After conditioning for 24 hours	After additional 24 hours without shaking	25 hours after conditioning
DI	8.65±0.05	9.41±0.05	9.42±0.05
5000 NaI	8.81±0.05	7.91±0.05	7.9±0.05
5000 NaCl	9.07±0.05	8.29±0.05	8.31±0.05
5000 NaBr	9.14±0.05	8.44±0.05	8.44±0.05

As shown in Table 5, the pH of calcite in deionized water is 9.42 which is higher than pH of the deionized water used (pH = 7). Dissolution of calcite is believed to be the reason for the increased pH value.

3.2.3 Calibration Measurements

Zeta Potential measurements were conducted right after the measurements of pH values. However, before conducting the actual measurement of prepared suspensions, the zeta potential electrode assembly was first conditioned in the same brine in which the

suspensions were prepared. Conditioning of electrode assembly was done with 1 run of 50 cycles, while keeping the voltage and frequency settings of the instrument at auto. The auto settings of the instrument allow instrument to optimize the voltage and frequency that best fit for a particular sample. Around 1.5 ml of prepared solution was placed into clean plastic cuvette by using a syringe and a needle with a built-in 5-micron filter. Then, the electrode assembly was carefully placed into the solution, while holding the cuvette at 45^{o} to avoid trapping of air inside the cuvette. Zeta Potential measurements were conducted with 5 runs of 25 cycles each and instrument settings were set to auto voltage and 20 Hz frequency. After each measurement, the samples were visually examined to check for any sample degradation. Each experiment was repeated 3 times to assure repeatability. A pH of 7.5 was maintained by adding 0.1 molar HCl or NaOH solution. pH was measured before and after each measurement. All zeta potential measurements were conducted at 25^{o}C.

Table 6: Measured ζ values of calcite treated with different salt solutions at two different conditioning times at pH 7.5.

Calcite treated with	ζ after 24 hours conditioning	ζ after 48 hours conditioning
DI Water	-4.70 ± 0.23	-4.50 ± 0.17
5000 ppm NaI	-11.81 ± 0.13	-11.85 ± 0.29
5000 ppm NaBr	-11.27 ± 0.15	-11.30 ± 0.32
5000 ppm NaCl	-6.85 ± 0.35	-6.83 ± 0.19

Time lapse zeta potential measurements of calcite suspensions were done after each 24 hour consecutively as shown in Table 6, and no significant changes in the zeta potential values were observed after 24 hours. This shows that 24 hours is a reasonable amount of time to get stabilized zeta potential values. It is also observed from the study of Alotaibi et al. [99] that 24 hours conditioning time is adequate.

Table 7: Measured ζ values of unmodified calcite and carbonate in de-ionized water for two separate pH values at 25ºC and its comparison with zeta potential results found in the literature [100]**.**

ZETA POTENTIAL MEASUREMENTS		
	Literature [100]	**Experiment**
Calcite	-12.5 @ pH 9.5±0.05	-9.5±0.82 @ pH 9.4±0.05
Carbonate	-14.58 @ pH 9.6±0.05	-13.5±0.5 @ pH 9.4±0.05
Calcite	-4.16 @ pH 7.2±0.05	-4.5±0.3 @ pH 7.2±0.05
Carbonate	-10.4 @ pH 7.3±0.05	-8.5±0.3 @ pH 7.5±0.05

Table 7 shows the preliminary results of unmodified calcite and carbonate rock particles suspended in de-ionized water at different pH values. It is found that the results obtained were close to the values found in the literature. This confirms the reliability of the experimental procedure and the instrument calibration. The variation could be due to the rock compositions.

3.3 Preparation of Modified Calcite and Carbonate Outcrop Rock

5 g of each calcite and carbonate outcrop rock samples were placed into 50 ml of different model oils separately. Suspensions were then conditioned under room temperature for 24 hours in a multi wrist shaker. The 24 hours have been reported to be sufficient time for modifying the calcite and carbonate outcrop rock and adequate for adsorption of polar components of model oil onto the rock surface [49], [101]. After conditioning, vacuum filtration was done using a 0.7 μm filter paper to produce the modified solid rock particles.

In order to confirm whether the rock particles are water wet or oil wet (after modifying with model oils), a floatation test as described in Kasha [100] and Dubey [102] was conducted by adding 0.25 g of each modified/unmodified calcite and carbonate samples separately in 5ml distilled water into clean glass vials. The suspension was allowed to

remain stand for 48 hours without conditioning. It was observed that modified powder of calcite and carbonate were floating at the surface in distilled water indicating that the powder has become completely oil wet. Figure 4 and Figure 5 show the modified/unmodified calcite and carbonate outcrop rock suspensions in distilled water before conditioning.

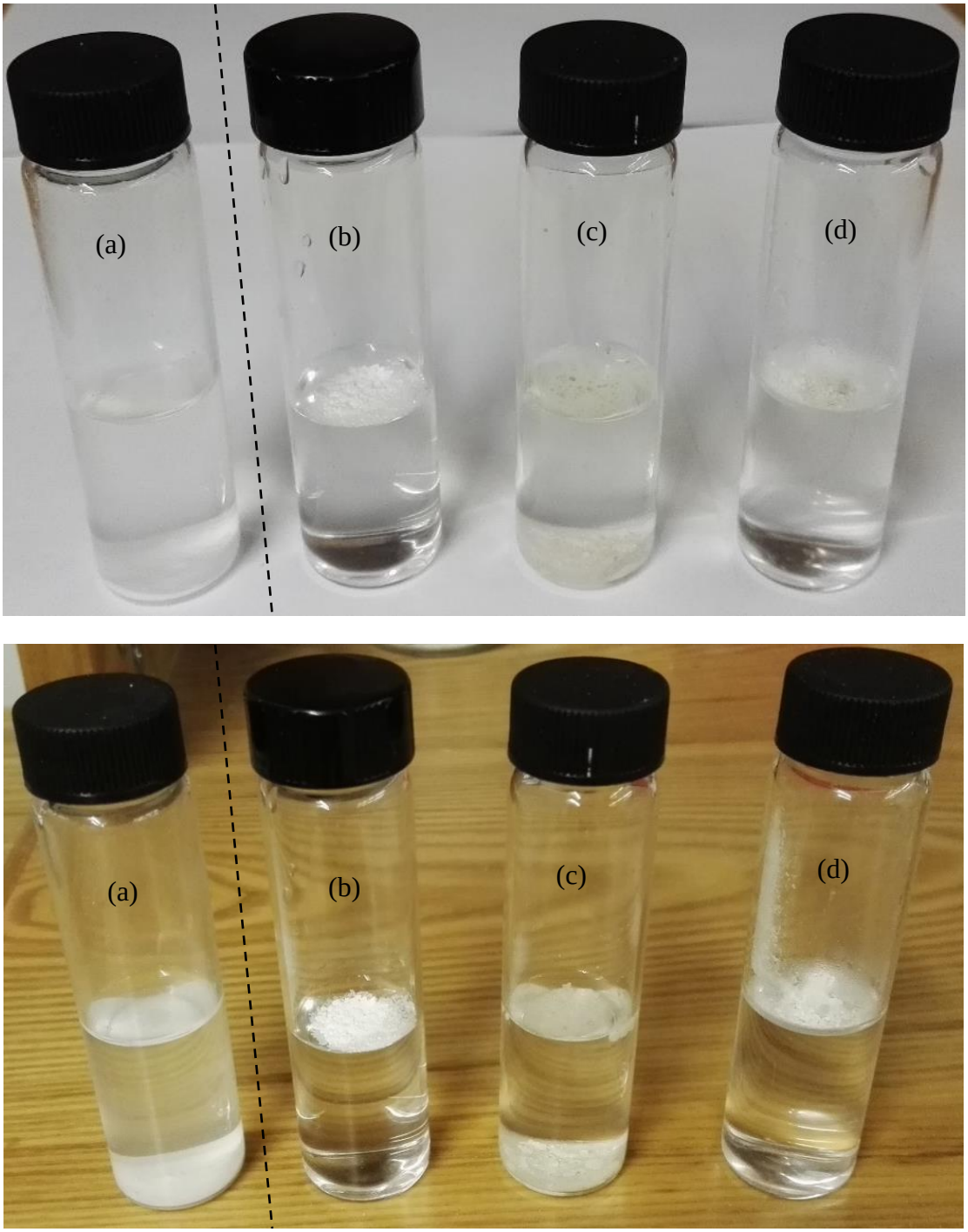

Figure 4: (a) Unmodified calcite (b) calcite modified with model oil (TS) (c) calcite modified with model oil (TA) (d) calcite modified with model oil (TSA) and suspended in deionized water

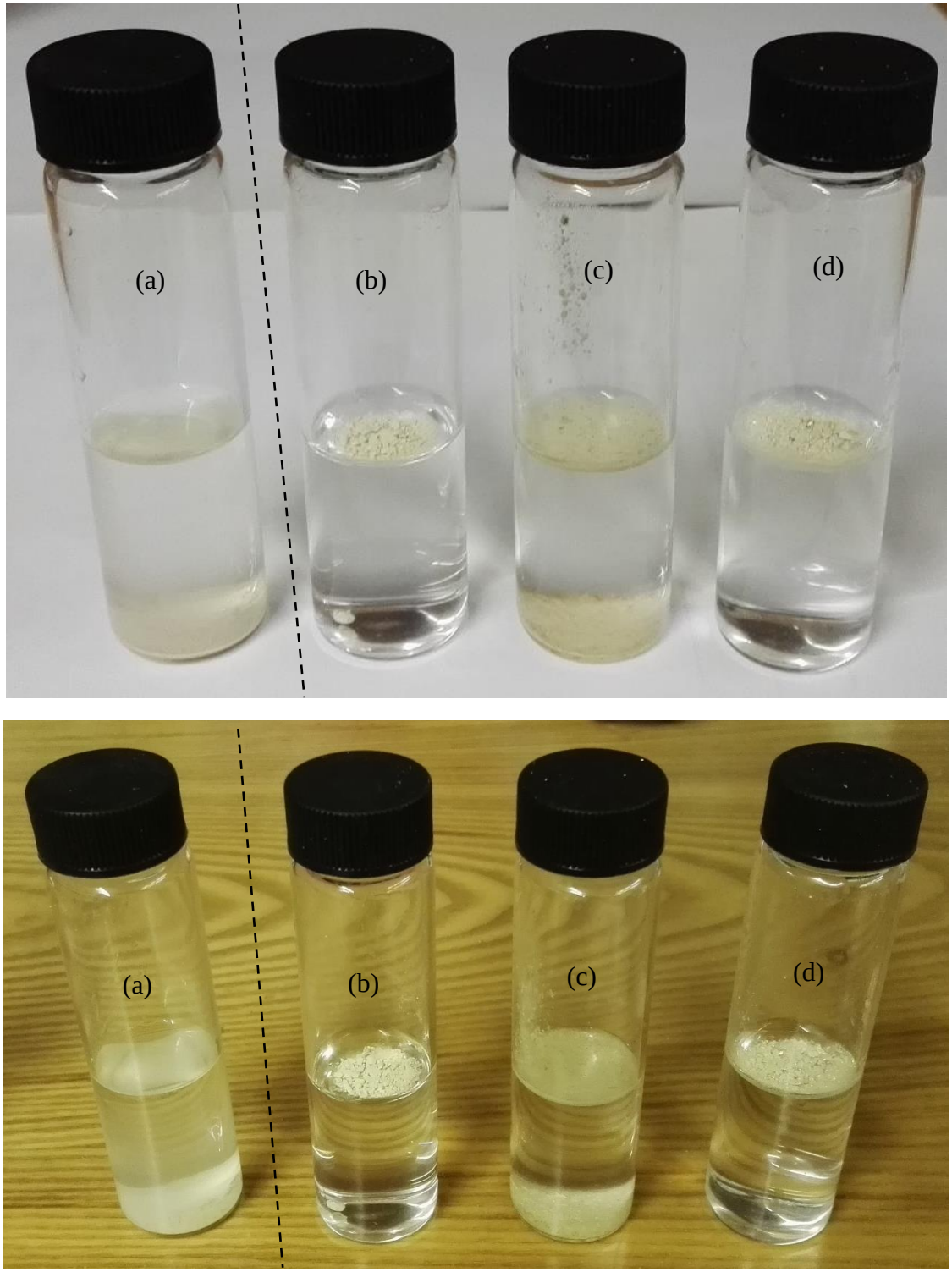

Figure 5: (a) Unmodified carbonate outcrop (b) carbonate outcrop modified with model oil (TS) (c) carbonate outcrop modified with model oil (TA) (d) carbonate outcrop modified with model oil (TSA) and suspended in deionized water

It is observed from Figure 4 and Figure 5 that unmodified calcite and carbonates outcrop particles settle to the bottom. Modified rock particles floated at the surface due to the adsorbed surface active components which indicates that the rock particles become oil wet. Particles with adsorbed model oil (TA) partially floated at the surface and it is ascribed as a partial adsorption of components from the asphaltene.

3.4 Procedure for Characterization of Rock Samples using SEM-EDS and Raman Spectroscopy

SEM (Scanning Electron Microscope) is used for the qualitative description of mineralogy, grain texture, its size and shape. Whereas EDX or EDS (Energy Dispersive X-ray Spectroscopy) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It measures the elemental composition of a point or an area of interest on the surface. Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.

In this study, unmodified and modified rock samples with model oil (TS) were analyzed using SEM-EDS to observe topographic and compositional changes at the rock surface. Crushed and grinded rock samples were used for all SEM-EDS analysis. Modified rock samples were obtained as described in the previous section. Modified calcite rock samples were further analyzed using SEM-EDS after conditioning in selected brine samples. All SEM-EDS measurements were performed under room temperature with accelerating voltage of 20 kV and resolutions of 5 and 500-micron. Raman spectroscope is used to analyze brine sample after conditioning with modified calcite rock (TS), followed by filtration to observe the release of stearic acid from the rock surface.

Figure 6 presents a schematic diagram of the approach used to understand the adsorption and desorption of ions from the brines and the sorption of oil polar component on the rock surface by using SEM-EDS and Raman spectroscopy.

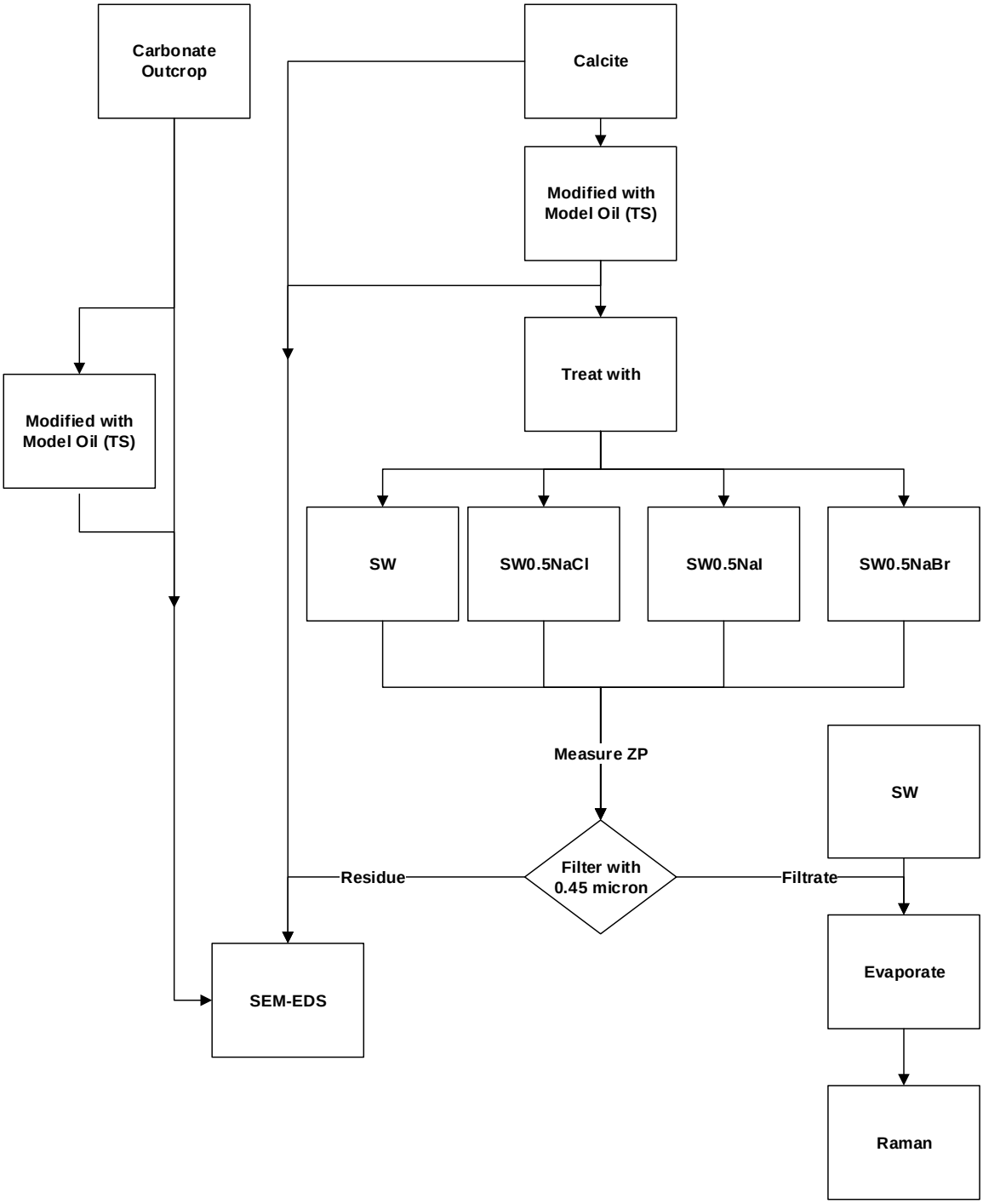

Figure 6: Flow chart of SEM-EDS and Raman measurements

CHAPTER 4

RESULTS AND DISCUSSION

Zeta potential varies with the change in pH value of the suspensions and that, consequently alters the brine/rock interaction. In order to compare the interaction of different brines with the rock surface either unmodified or modified with model oils, the effect of pH should be eliminated by using a constant pH value of the suspensions. Thus, it will reflect the interaction of rock with different brines. Many studies [103]–[105] reported that the pH values lie in the range between 6-8, under reservoir conditions. Therefore, in this study, a constant pH value of 7.5 is chosen to compare the behavior of rock surfaces, independent of pH value. To analyze the effect of calcite and carbonate outcrop in DI water, zeta potential for both rocks were measured in deionized water at a constant pH value of 7.5 as shown in Figure 7.

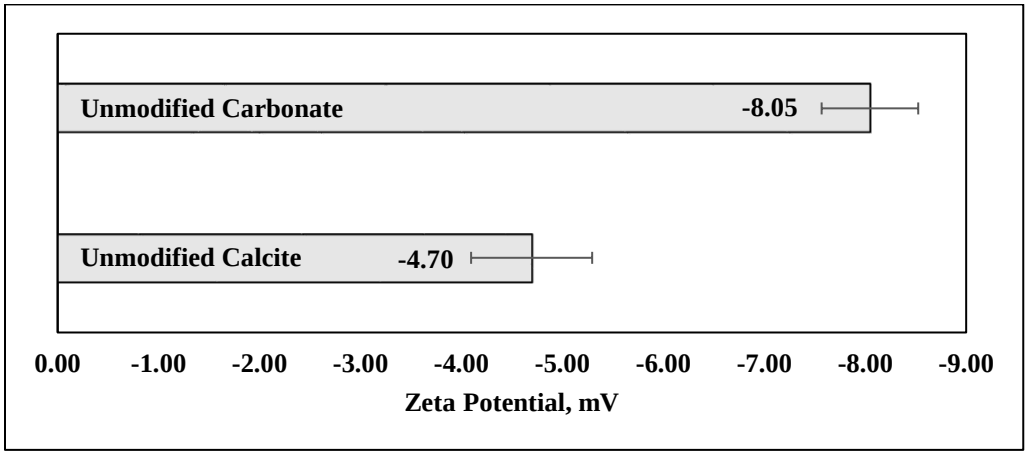

Figure 7: Zeta potential of unmodified calcite and carbonate outcrop rock at 25ºC in DI water at 7.5 pH.

The zeta potential of unmodified calcite and carbonate outcrop particles suspended in de-ionized water are shown in Figure 7. Both rocks show negative charge at pH 7.5 in de-ionized water. These results are consistent with the results reported in the literature: calcite (-5.33 mV at pH of 7.5) and carbonate rock (-10.4 mV at 7.3 pH) [32]. Calcite dissolution [106],[107] is believed to be the reason behind the negative ζ values and these observations are in-line with what is observed from this study as presented in section 4.3. Calcite particles dissociates into Ca^{2+} and CO_3^{2-} upon interaction with DI water [108]. When carbonate rock particles come in contact with DI water, Ca^{2+} ions start to dissolve in the water and continues to dissolve in the water and dissolution continues until it reaches equilibrium with the surrounding ions such as Ca^{2+}, CO_3^{2-}, HCO_3^- and OH^-. The solubility of calcite also depends on the amount of dissolved CO_2 that comes from the atmosphere. The addition of CO_2 in deionized water produces carbonic acid that lowers the pH value and increases the calcite dissolution rate. Since all experiments were performed carefully in a closed system to have minimum interaction of atmospheric CO_2 with the samples, the pH value stabilizes after the dissolution reached equilibrium. Upon dissolution of calcite in DI water, the following reactions take place [109]:

$$CaCO_3\,(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}\,(aq) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$CO_3^{2-}\,(aq) + H_2O\,(l) \rightarrow HCO_3^-(aq) + OH^-(aq) \quad \ldots\ldots\ldots\ldots (2)$$

In the absence of CO_2, Ca^{2+} ions preferentially leave the calcite surface that makes the surface negatively charged. A similar observation is reported by Douglas and Walker [110] in which they used CO_2 free water with calcite. According to them, the negative charge on calcite surface occur by the preferential leaving of Ca^{2+} ions from the calcite surface,

leading to a negatively charged calcite surface. Figure 8 shows the pictorial presentation of the mechanism involve when calcite rock particles are treated with DI water. When calcite rock particles interact with DI water, Ca^{2+} leaves the calcite surface and the overall accumulation of negative charge increases in the diffuse layer, making the zeta potential value negative.

For the studied samples, the ζ value is more negative for the carbonate outcrop than for calcite, which is most likely due to the slight difference in calcite content. This observation is in agreement with the study conducted by Chen et al. [80]. They reported that increasing the calcite content is benefit to the increase of the zeta potential, that is, the high content calcite results in the high ζ value. Moreover, Mahani et al. [111] also observed the same trend through zeta potential measurements of limestone and calcite particles conditioned in different brines such as sea water, formation water, 25 times diluted sea water and sea water plus 4 times increase in original SO_4^{2-} concentration in sea water. They reported that pure calcite particles adsorb less negative ions than limestone particles, and consequently lower the magnitude of zeta potential for calcite than for limestone particles. It is possible that the additional negative charge in carbonate outcrop rock could be due to the presence of Quartz (SiO_2) which exhibits negative charge around the particle as reported in the literature [112], [113]. Furthermore, Strand et al. [51] investigated three different types of chalk samples with varying percentages of silica, 1.4 wt%, 2.8 wt% and 6.3 wt%. They observed similar wetting properties for the chalk sample with 1.4 wt% and 2.8 wt% silica. However, chalk with 6.3 wt% silica showed quite different wetting properties. They observed that the rock tends to be more water-wet when the silica content increases in the chalk samples. In another study, Smani et al. [114] reported a negative zeta potential of

carbonate rock mainly comprised of calcite with traces of quartz. Presumably, the percentage of silica in carbonate rock leads to additional negative charge that eventually expands the double layer around charged particle, which consequently increases the magnitude of the negative zeta potential as compared to pure calcite.

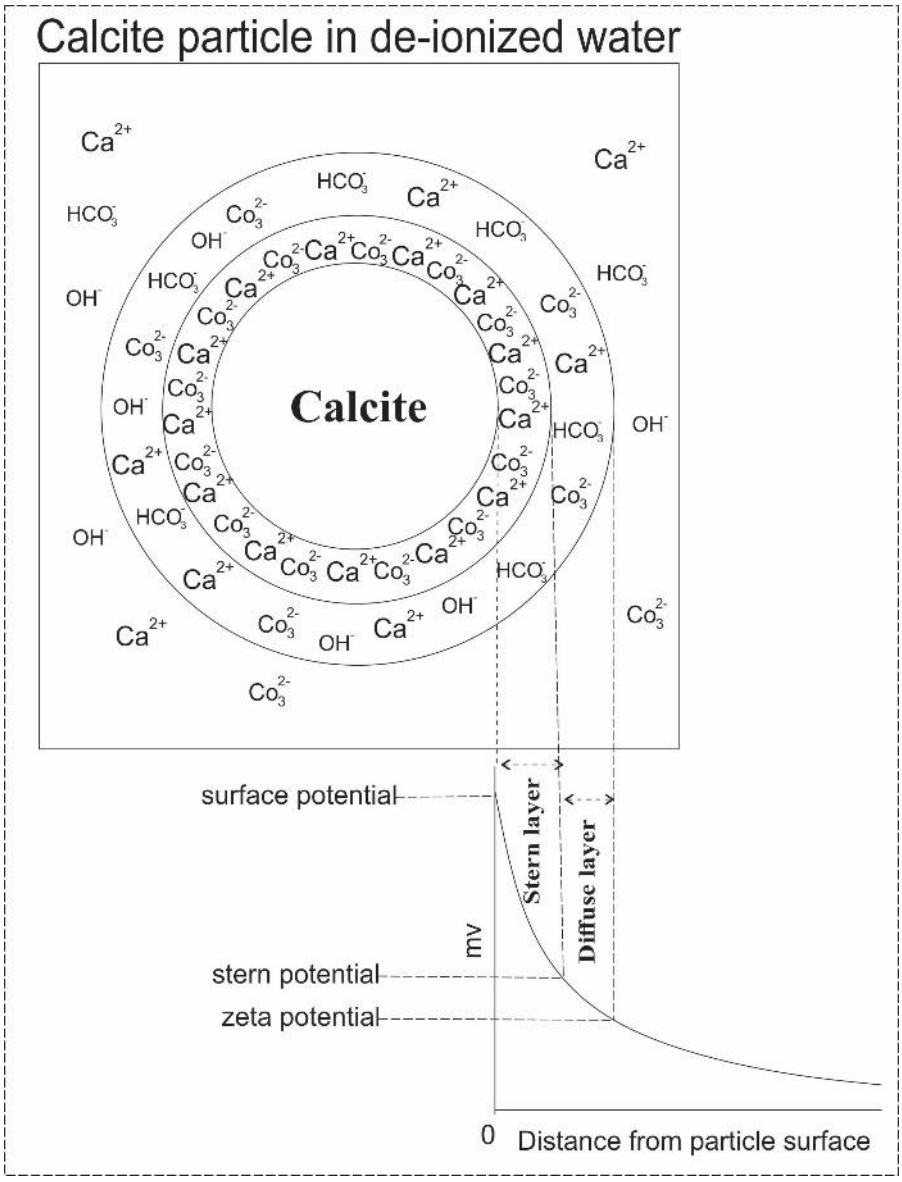

Figure 8: Schematic of the mechanism when calcite particle conditioned in DI water

4.1 Unmodified and modified calcite particle suspensions in deionized water

To investigate the effect of different model oils on the surface of calcite particle, zeta potential was measured for rocks modified with model oils and conditioned in deionized water as shown in Figure 9.

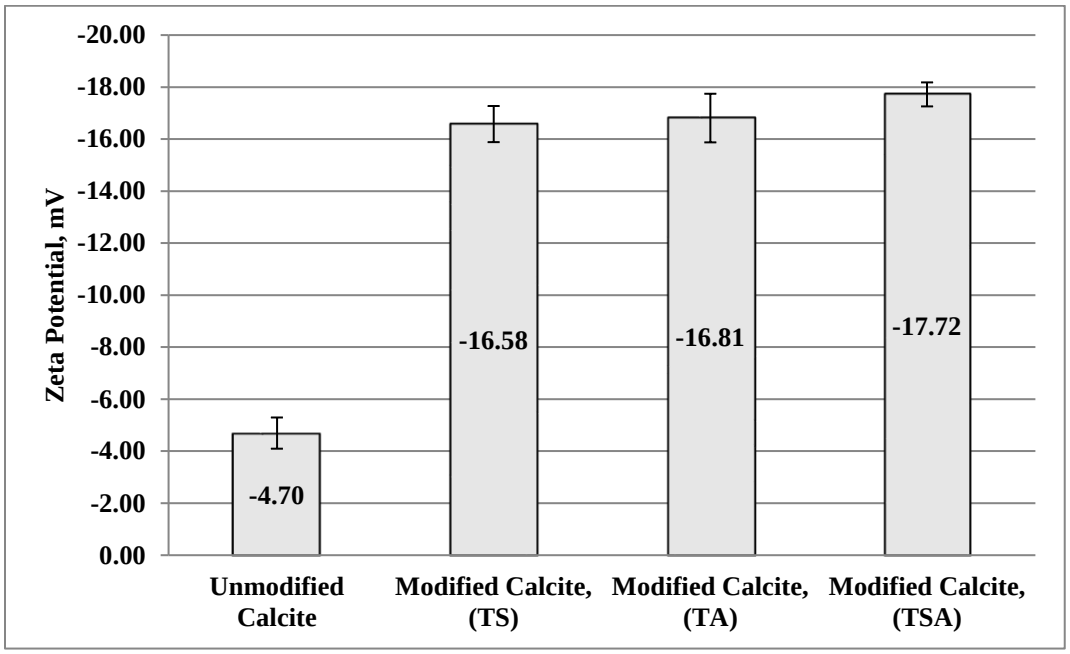

Figure 9: ζ of unmodified rock and all modified calcite rock particles suspended in deionized water at 7.5 pH at 25ºC temperature

All modified calcite particles show higher negative charge than unmodified calcite as shown in Figure 9. The increase in negative charge comes from the adsorption of polar model oil components stearic acid and asphaltene [32]. Gonzalez and Middea [115] studied the impact of three different samples of asphaltenes onto calcite rock and they found that all ζ values were negative. Moreover, the values of ζ were in the range of -14 to -16 mV which is close to our measurement for ζ of modified calcite with model oil (TA) that resulted in -16.58 mV. Comparing the results of modified rocks with model oil (TS) and with model oil (TA) show that the adsorption of asphaltene on calcite particles produced slightly more negative charge as compared to stearic acid adsorption on calcite rock

particles. It should be noted that the different concentrations of asphaltene and stearic acid in model oils (TS and TA) could also influence the magnitude of zeta potential. Tabrizy et al. [116] reported that the asphaltene makes the calcite rock more oil wet than stearic acid, as determined by new proposed wettability index measurements. Gonzalez and Middea [115] also reported wettability change due to adsorption of asphaltene on the rock surface. However, they observed insignificant role of asphaltene in altering the surface charge on the rock surface. Despite that, there are several studies reporting a negative charge on asphaltene dispersed in 1mM $NaNO_3$, in the pH range between 4.5-10.3 [92] and in the pH range between 3.5-10.5 [117], assuming that neither sodium nor nitrate adsorb at the solid asphaltene-aqueous interface [118], [119]. The zeta potential of asphaltene is negative in aqueous media above pH 5 [120]–[123]. In another study, Taqvi et al.[79] observed an increase of negative zeta potential upon addition of asphaltenic solution in aqueous limestone rock that was mainly comprised of calcite. It is now clear from the reported studies that asphaltene exhibits negative charge either present as a solid in an electrolyte solution (eg. $NaNO_3$) or adsorb on the rock surface, which is also in agreement with this study.

It is also observed from this study that the combined effect of stearic acid and asphaltene (TSA) yielded slightly more negative charges than model oils (TS and TA) on calcite surface as shown in Figure 9. Chukwudeme et al. [124] and Tabrizy et al. [116] reported that the combined effect of stearic acid and asphaltenes makes the calcite surface more oil wet than only one polar component, as measured by contact angle and wettability index, respectively. The zeta potential of modified rock (TSA) is slightly higher than the modified rock (TA), considering that the model oil (TSA) contains the same amount of stearic acid

and asphaltene as it is present in model oil (TS) and model oil (TA). It is attributed that the individual effect of stearic acid and asphaltene is not added up in the model oil (TSA), so we can infer that there is competition between both polar components to adsorb on the limited sites of the calcite surface.

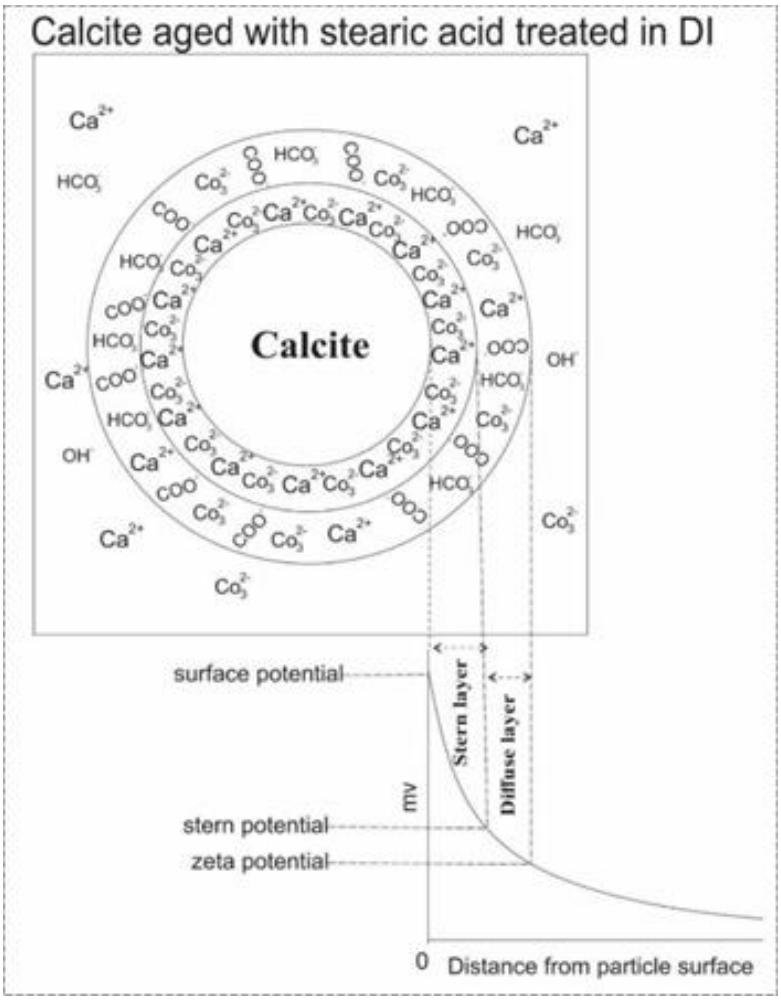

Figure 10: Schematic of the mechanism when modified calcite (TS) conditioned in DI water

Figure 10 shows the pictorial presentation of the mechanism involve when calcite rock modified with model oil (TS) is interacted with DI water. It is reported in the literature [125] that stearic acid adsorbs chemically on the calcite surface and forms a calcium

carboxylate complex [126]. When modified rock (TS) is treated with DI water, we propose two possible scenarios to understand the mechanism:

1) Ca^{2+} ions leave the calcite surface along with the adsorbed stearic acid as a result of calcite dissolution in DI water and produce a deficiency of positive charge on the surface. Consequently, the zeta potential becomes more negative as compared to corresponding zeta potential value of unmodified calcite in DI water because of the remaining negative adsorbed ions such as HCO_3^-, CO_3^- and OH^-.
2) The adsorption of polar species of stearic acid ($\sim COOH^-$) on the opposite charge of Ca^{2+} increased the overall negative charge in the diffuse layer.

If the first proposed mechanism is the active mechanism, the zeta potential values should be similar to the values of unmodified calcite in DI water. However, the value is -16.58±0.7 mV for the modified calcite (TS) while it is -4.7±0.6 mV for the unmodified calcite in DI water. The large difference in values supports the second proposed mechanism. The removal of Ca^{2+} ion along with stearate could be possible as pointed out in the first proposed mechanism, however the second mechanism is the dominant one in this case. It means that the increase of negative zeta potential on modified calcite rock particles is the result of adsorption of polar oil components from the model oils and these components were not released when modified rocks were conditioned in DI water. That's why some studies haven't shown potential in using DI water with modified rock to alter the wettability toward more water wet [49], [77].

4.2 Unmodified and modified carbonate outcrop particles treated with deionized water

To investigate the effect of different model oils on the surface of carbonate outcrop particle, zeta potential was measured for rocks modified with model oils and conditioned in deionized water as shown in Figure 11.

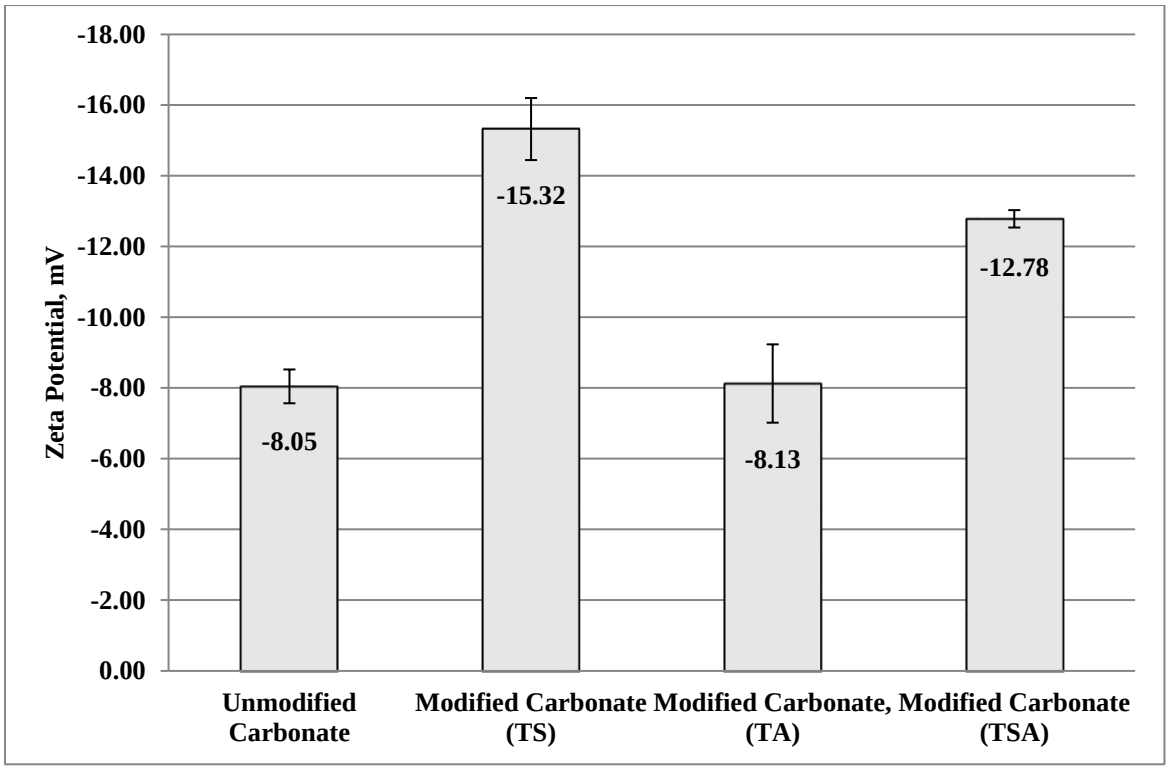

Figure 11: ζ of unmodified rock and all modified carbonate rock particles suspended in deionized water at 7.5 pH at 25ºC temperature

Modified carbonate rock particles (TS and TSA) yielded more negative charge than unmodified carbonate. Unlike calcite, the adsorption of stearic acid on carbonate outcrop showed highest negative zeta potential value as compared to other modified carbonate outcrops in DI water. For carbonate outcrop rock modified with model oil (TA), the increase in negative zeta potential was the lowest as compared to other modified rock

particles and showed a zeta potential similar to the ζ value of unmodified rock particle. We can assume that the calcite dissolution of modified carbonate rock (TA) in DI water resulted in desorption of asphaltenes from the rock surface. Another explanation for the unchanged zeta potential value compared to unmodified carbonate would be that there was no initial adsorption of asphaltene onto the carbonate surface. Also, the floatation test showed that the adsorption of asphaltene on the carbonate surface was lower than adsorption of stearic acid.

Comparing the results of calcite and carbonate outcrop, modified calcite rock (TA) in DI water showed increase in magnitude of zeta potential as compared to unmodified calcite rock, while the effect is not significant in case of modified carbonate outcrop (TA) as compared to unmodified carbonate outcrop. It is shown in Figure 7 that the absolute negative value of zeta potential of unmodified carbonate outcrop is higher than unmodified calcite rock in DI water. Thus, because of the less negative charge on the calcite as compared to carbonate outcrop rock surface, asphaltene tends to adsorb more on calcite rather than carbonate outcrop. In another study, Gonzalez et al. [127] observed that asphaltenes produced moderate changes in the electrical properties of the mineral-solution interface. However, these changes were not evident for minerals exhibiting a large negative zeta potential.

The results of modified carbonate (TSA) in DI water also shows that as if there is no adsorption of asphaltene, the results of modified rock (TSA) would have to be the same as modified rock(TS). The value of modified rock (TSA) was less than modified rock (TS) and higher than modified rock (TA). It is most likely the combined effect of stearic acid and asphaltene, considering that asphaltene tends to adsorb less on carbonate outcrop and

would hinder the adsorption of stearic acid on the rock. Thus, the overall charge on modified rock (TSA) reduced as compared to modified rock (TS) in DI water.

4.3 Effect of monovalent ions on the surface charge of unmodified and modified calcite and carbonate outcrop

To evaluate the effect of different anions on the surface of unmodified rocks, zeta potential was measured for both unmodified rocks, followed by conditioning in different sodium brines as shown in Figure 12.

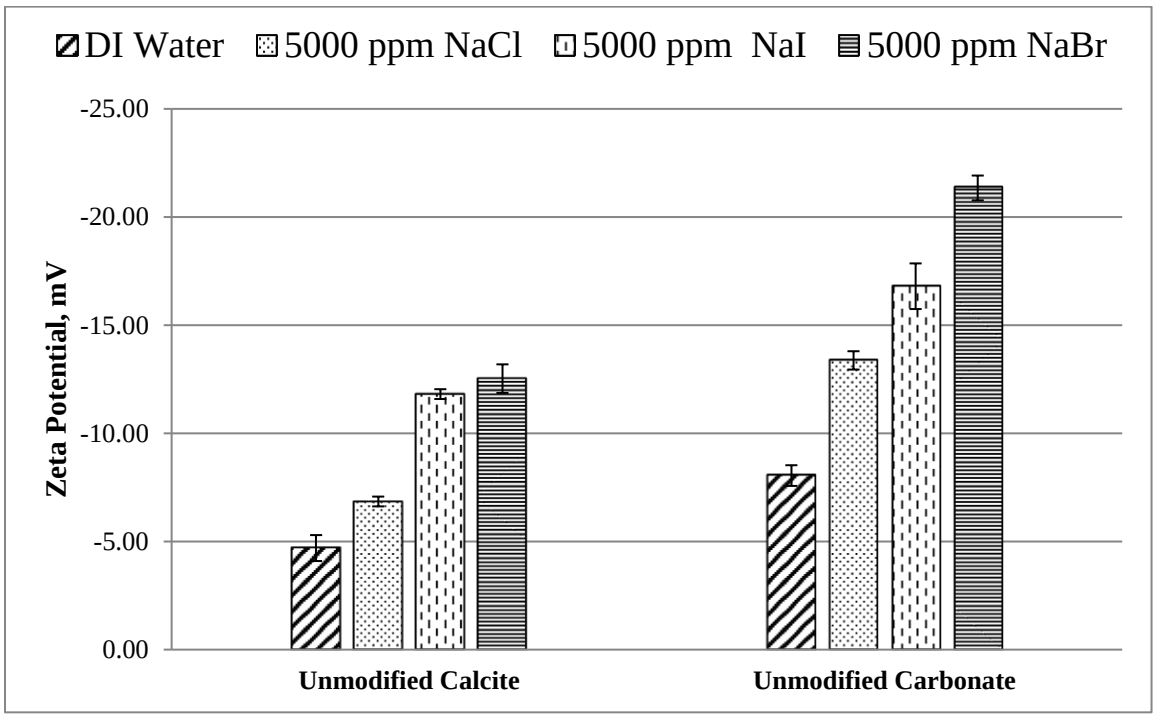

Figure 12: ζ of unmodified calcite and carbonate outcrop rock particles treated with different brines at 7.5 pH and 25°C.

It can be seen that zeta potential shows the same trend in response to the investigated ions for the case of unmodified calcite and unmodified carbonate outcrop suspensions. Ahmed and Hisham [128] reported zeta potential of -9.8 mV at 9.5 pH for calcite particles conditioned in 5000 ppm NaCl, while Saraji et al. [129] reported -13.63 mV at 8.50 pH and -5.02 mV at 9.17 pH for calcite particles conditioned in 526 ppm and 52,500 ppm

NaCl, respectively. Whereas Zhang and Austad [30] reported zeta potential of -8 mV at 8.4 pH for calcite particles conditioned in 33,390 ppm NaCl. It is observed that the reported measurements are close to our measurements for calcite in 5000 ppm NaCl i.e. -6.85±0.23 mV at 7.5 pH, considering that the zeta potential decreases with an increase in pH value and decrease in salinity. Alotaibi et al. [25] reported ζ of -21.6 mV at 7 pH for limestone particles conditioned in 5436 ppm NaCl. However, the zeta potential measured in this study for carbonate outcrop, conditioned in 5000 ppm NaCl, is -8.05±0.48 at 7.5 pH value. It is possible that the magnitude of zeta potential could vary with the different rock composition, experimental conditions and sample preparation procedures. However, it is consistent with the reported studies that the zeta potential on both rock surfaces, conditioned in 5000 ppm NaCl, is negative at pH value close to 7.5.

It is observed from Figure 12 that the magnitude of the negative zeta potential is increased from the case for NaCl over NaI to NaBr. Agudo et al. [106] observed more calcite dissolution in NaI solution than in NaCl, with both having a constant ionic strength (IS) of 0.1 M. They measured the calcite dissolution rate and etch pitch spreading rate by AFM on calcite chips, treated with different brines. During their study, they found that in the presence of a small concentration of NaCl (1 mM) in the surrounding medium, calcite dissolution is slightly higher than in deionized water, and at higher concentration (0.1M NaCl), the dissolution rate is further enhanced.

In order to confirm calcite dissolution for calcite rock incubated for 24 hours in the respective brines, the calcium ion concentrations of the brines after filtration of the calcite rock particles, using a 0.5-micron filter paper, were determined by using ICP-OES. Table 8 shows the calcium ion concentrations recorded in the filtered brines.

Table 8: Composition of ions in the filtrate of calcite rock equilibrated with deionized water and different salt solution (NaCl, NaBr, NaI) of 5000 ppm salinity

Filtrate of	Ca^{2+} ions (ppm)
Calcite + DI water	65.78
Calcite + NaCl	3981.25
Calcite + NaBr	2367.08
Calcite + NaI	1721.2

It is observed from Table 8 that the calcium ion concentration increased in brines, that were in contact with calcite rock, in the sequence DI water < NaI < NaBr < NaCl. The high concentration of Ca^{2+} ions resulting from dissolution of calcite in NaCl solution as compared to in the DI water system is in agreement with Agudo et al. [106]. While NaCl > NaI is in disagreement with Agudo et al [106]. A possible explanation is that they used a constant concentration of 0.1 M for all salts, while our brines ionic strength is varied in the sequence NaCl (IS=0.086 M) > NaBr (IS=0.049 M) > NaI (IS=0.033 M).

Comparing the zeta potential measurements with calcite dissolution as reported in Table 8, one would assume the same trend (NaCl > NaBr > NaI > DI) instead of NaBr > NaI > NaCl > DI, if calcite dissolution was the only mechanism leading to the change in zeta potential. However, the possible adsorption of NaI and NaBr on the calcite rock surface could produce more negative charge on the calcite surface. The ζ of NaI and NaBr show higher negative value than NaCl. Thus, we can conclude that adsorption of ions as well as calcite dissolution both play a major role in creating surface charge alteration on the rock. To confirm the adsorption of ions on the calcite surface, we measure the difference between initial concentrations of Cl^-, Br^- and I^- ions present in the original brine solutions and the final concentration of ions after treated with the rock surface; shown in Table 9.

Table 9: Difference between initial concentration of ions before adding calcite and final concentration of ions after equilibrating with calcite rock with different salt solution (NaCl, NaBr, NaI) of 5000 ppm salinity

Ions	**Different between initial and final concentration**
Cl^-	88 ppm
Br^-	1205 ppm
I^-	2533 ppm

It is determined from Table 9 that the adsorption of ions on the calcite surface takes place during conditioning with respective brines. Thus, it is clear that the increase in negative zeta potential, as shown in Figure 12, represents the combined effect of calcite dissolution and adsorption of ions on the rock surface. The adsorption of Iodide ions on the calcite surface has also been reported in the literature [130].

4.4 Comparison of modified calcite particles conditioned in 5000 ppm NaCl with modified calcite particles conditioned in DI water

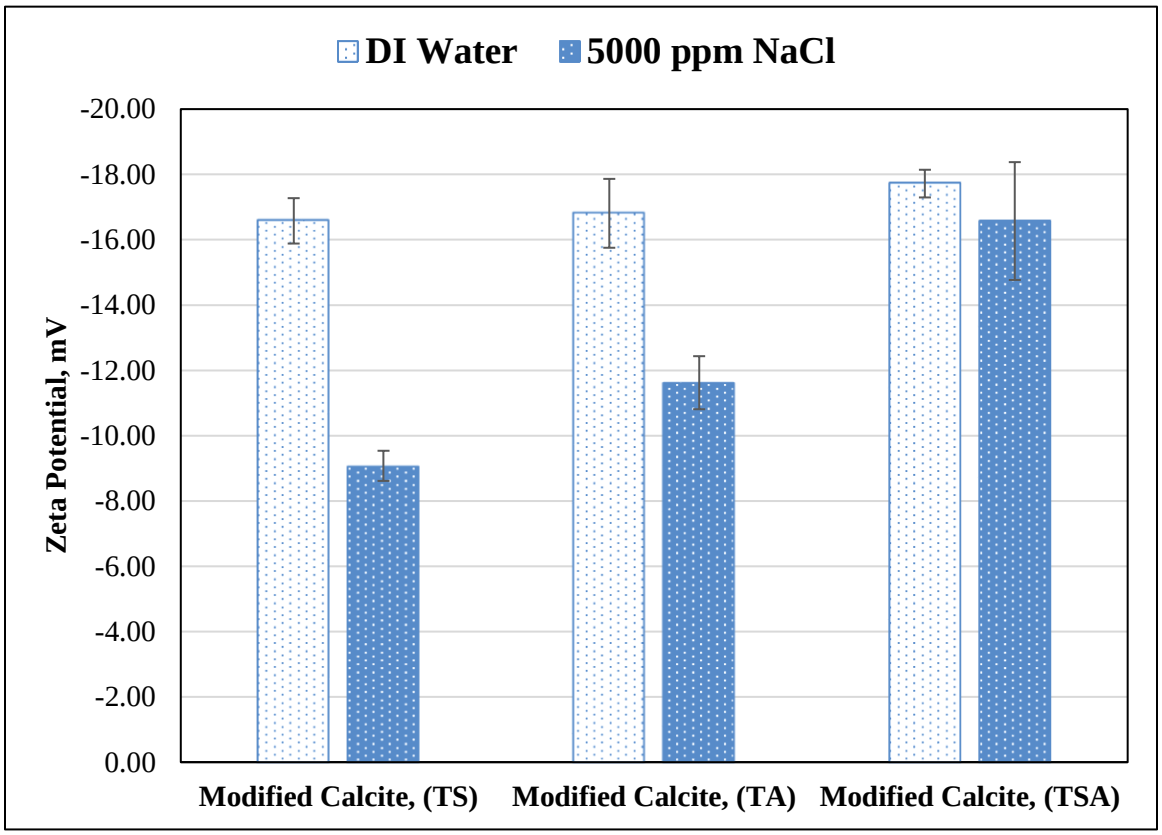

Figure 13: ζ values of modified calcite rock particles suspended in DI water and in 5000 ppm NaCl at 7.5 pH and 25°C

Figure 13 shows the ζ values of calcite rock particles modified with model oils and then treated with DI water and 5000 ppm NaCl. The ζ value of modified rock (TSA) is closed to the ζ value of modified rock (TSA) in DI water. It is attributed that the addition of NaCl did not release any model oil components from the modified calcite rock (TSA). The ζ values of modified rocks (TS and TSA) were lower than the corresponding values of zeta potential in DI water. It is possible that the addition of 5000 ppm NaCl released surface active species from the modified rocks (TS and TSA), that consequently reduced the magnitude of zeta potential. However, the combined effect of stearic acid and asphaltene,

that is the case of modified rock with model oil (TSA), was so strong that the 5000 ppm NaCl was not able to remove sufficient adsorbed components.

4.5 Comparison of modified calcite particles conditioned in 5000 ppm NaI with modified calcite particles conditioned in DI water

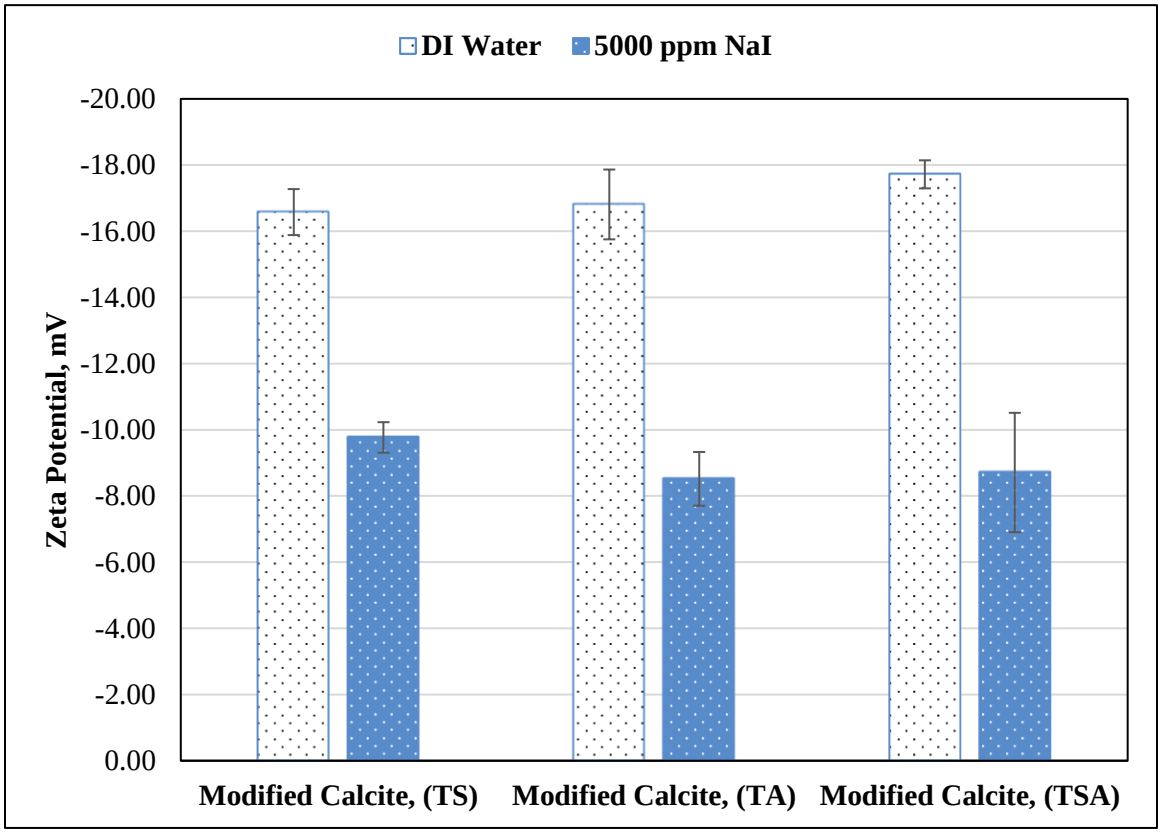

Figure 14: ζ values of modified calcite rock particles suspended in DI water and in 5000 ppm NaI at 7.5 pH and 25ºC

Figure 14 shows the ζ values of calcite rock particles modified with model oils and then treated with DI water and 5000 ppm NaI. It is observed that all modified calcite rocks showed consistent less negative ζ values as compared to the corresponding zeta potential values of modified calcite rocks in DI water. It is attributed that 5000 ppm NaI could have led to desorption of surface active compounds from the rock surface. Generally, the adsorption of surface active components from the model oils produces more negative

charge on the rock surface and when these components desorb from the rock surface, it is most likely that the negative charge will be reduced.

4.6 Comparison of modified calcite particles conditioned in 5000 ppm NaBr with modified calcite particles conditioned in DI water

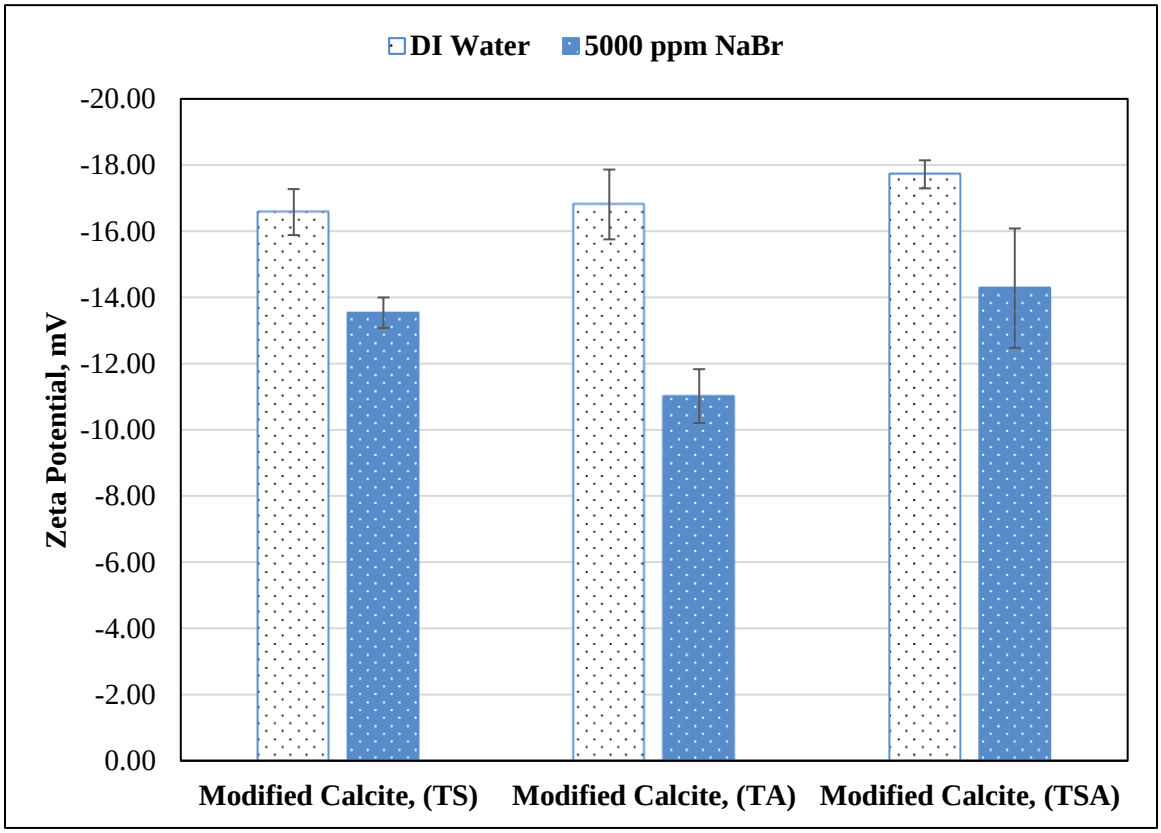

Figure 15: ζ values of modified calcite rock particles suspended in DI water and in 5000 ppm NaBr at 7.5 pH and 25°C.

Figure 15 shows the ζ values of calcite rock particles modified with model oils and then treated with DI water and 5000 ppm NaBr. It is observed that all modified calcite rocks showed consistent less negative ζ values as compared to the corresponding zeta potential values of modified calcite rocks in DI water. It is attributed that the treatment of modified rocks with 5000 ppm NaBr partially removed surface active components from the rock

surface. However, the effect is not as significant as it was observed with treatment of modified rocks with 5000 ppm NaI.

It is concluded, from the analysis of modified calcite rock particles treated with different low salinity brines, that 5000 ppm NaI is the most effective brine for modified calcite rock for altering the rock wettability toward less oil wet. Moreover, 5000 ppm NaBr is not as effective as 5000 ppm NaI, while 5000 ppm NaCl is the least effective brine as observed from the zeta potential measurements.

The decrease in negative charge on the modified rock surface is only possible when the polar oil components release from the rock surface. It was determined earlier that all modified rock particles were floating (partially or fully) at the top of water level (DI water) before conditioning which means particles had been modified with model oil components and modified rock particles were floating because of the hydrophobic nature of the model oil components. So, in order to verify the desorption of oil components from the rock surface, we conditioned the modified rock particles with 5000 ppm NaI and observed any floating particles. It is shown in Figure 16 that conditioning in 5000 ppm NaI showed no floating particle. It is attributed that conditioning of modified calcite rock particles released oil components from the rock surface and altered the rock wettability toward less oil wet.

Hence, the decrease in negative zeta potential value of modified rocks when conditioned in different brines exhibits release of oil components and the lowest negative charge is observed by conditioning of modified calcite rock in 5000 ppm NaI. Thus, 5000 ppm NaI is considered to be the most effective brines based on zeta potential measurements for the modified calcite rock.

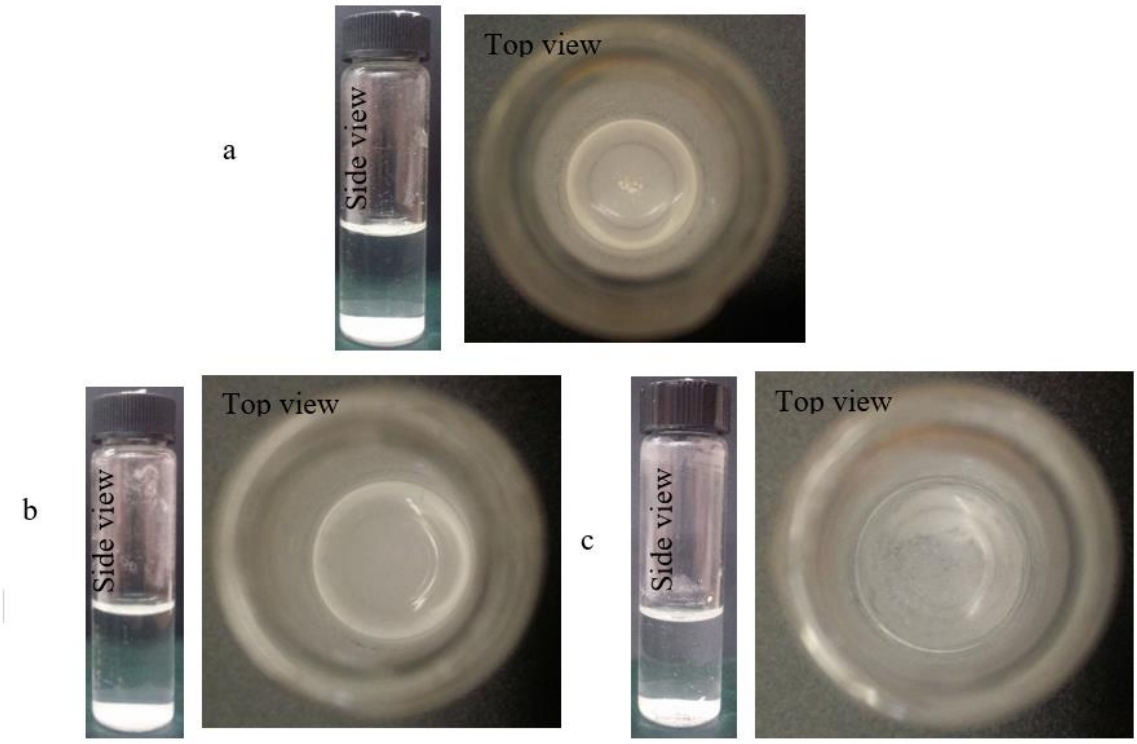

Figure 16: Floatation test of calcite particles modified with (a) model oil (TS), (b) model oil (TA) and (c) model oil (TSA) and conditioned in 5000 ppm NaI

4.7 Comparison of modified carbonate outcrop particles conditioned in 5000 ppm NaCl with modified carbonate outcrop particles conditioned in DI water

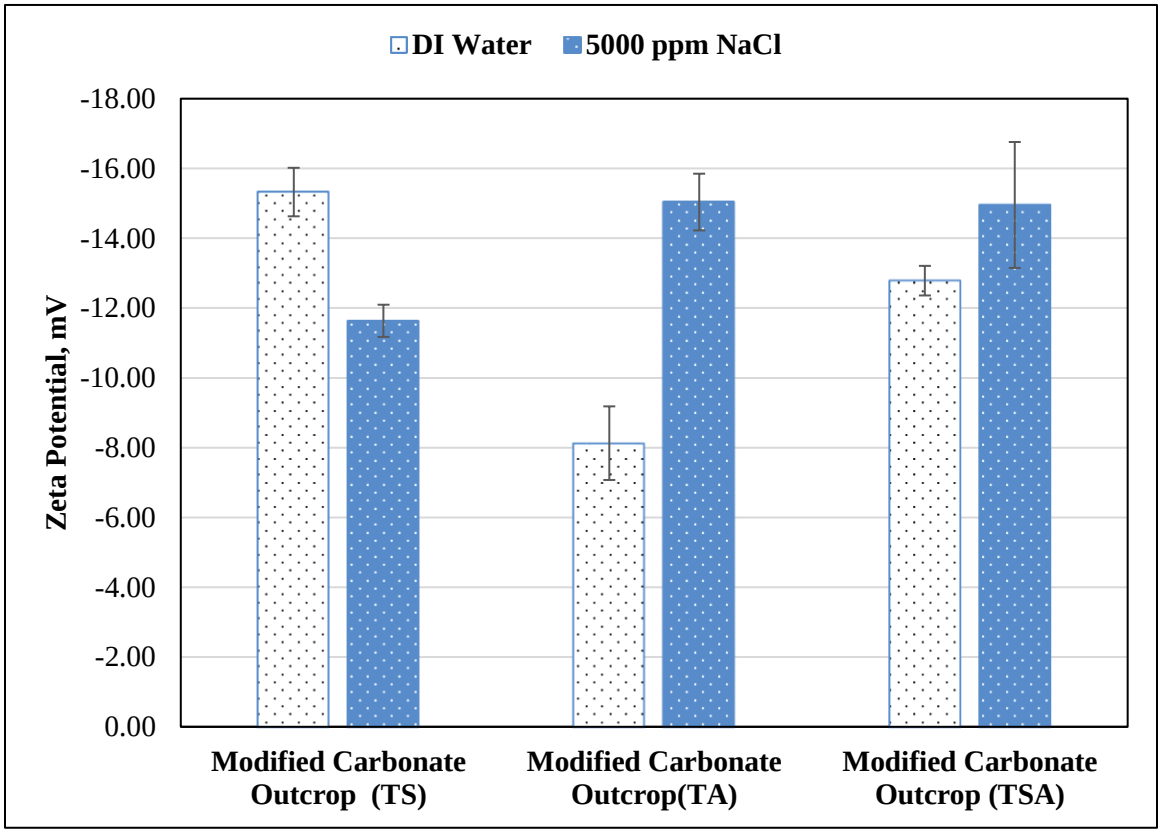

Figure 17: ζ values of modified carbonate rock particles suspended in DI water and in 5000 ppm NaCl at 7.5 pH and 25°C.

Figure 17 shows the ζ values of carbonate outcrop rock particles modified with model oils and then treated with 5000 ppm NaCl. For the case of modified carbonate outcrop treated with 5000 ppm NaCl, it is observed that the ζ values of modified rocks (TA and TSA) increased as compared to the corresponding ζ values of modified rocks (TA and TSA) in DI water. It is most likely that the adsorption of chloride ions on the modified rocks (TA and TSA) enhanced the negative zeta potential values. The ζ value of modified rock (TS) decreased as compared to the corresponding ζ value in DI water. It is possible that the addition of 5000 ppm NaCl released some adsorbed polar oil components from the rock surface, that lowered the zeta potential value.

4.8 Comparison of modified carbonate outcrop particles conditioned in 5000 ppm NaI with modified carbonate outcrop particles conditioned in DI water

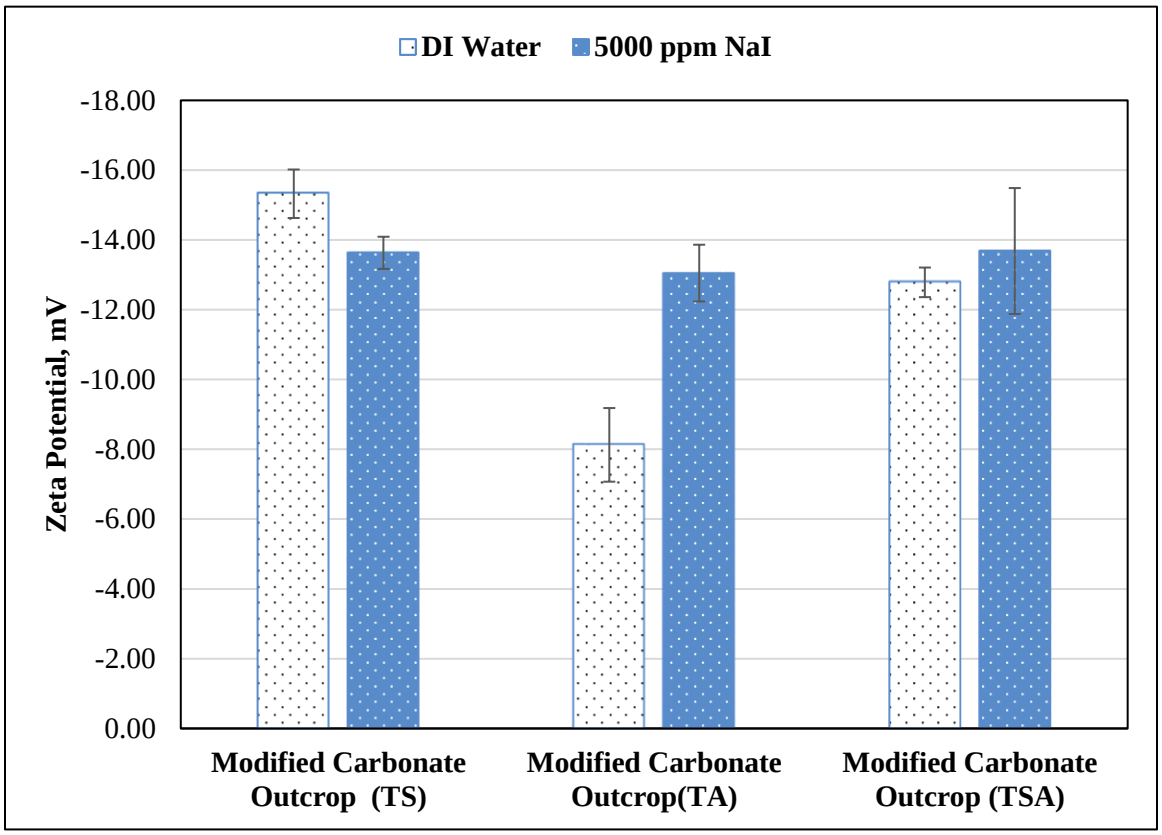

Figure 18: ζ values of modified carbonate rock particles suspended in DI water and in 5000 ppm NaI at 7.5 pH and 25°C.

Figure 18 shows the ζ values of carbonate outcrop rock particles modified with model oils and then treated with 5000 ppm NaI. It is observed that the ζ value of modified rock (TA) is higher than the corresponding value in DI water, which is attributed to the adsorption of iodide ions on the rock surface that increased the magnitude of zeta potential. The ζ value of modified rock (TS) in 5000 ppm NaI is lower than the corresponding value in DI water. It is possible that the conditioning of modified rock (TS) partially removed some adsorb surface active components that reduced the ζ value. The ζ value of modified rock (TSA) in 5000 ppm NaI is similar to the corresponding ζ value in DI water. In this case, two possible scenarios can be highlighted. It is expected that the process of adsorption of iodide ion on

the rock surface and the removal of stearic acid occurred simultaneously, that balanced the overall charge on the rock surface. It is also possible that the combined effect of adsorbed stearic acid and asphaltene was so strong that the conditioning of modified rock (TSA) in 5000 ppm NaI did not release model oil components from the rock surface.

4.9 Comparison of modified carbonate outcrop particles conditioned in 5000 ppm NaBr with modified carbonate outcrop particles conditioned in DI water

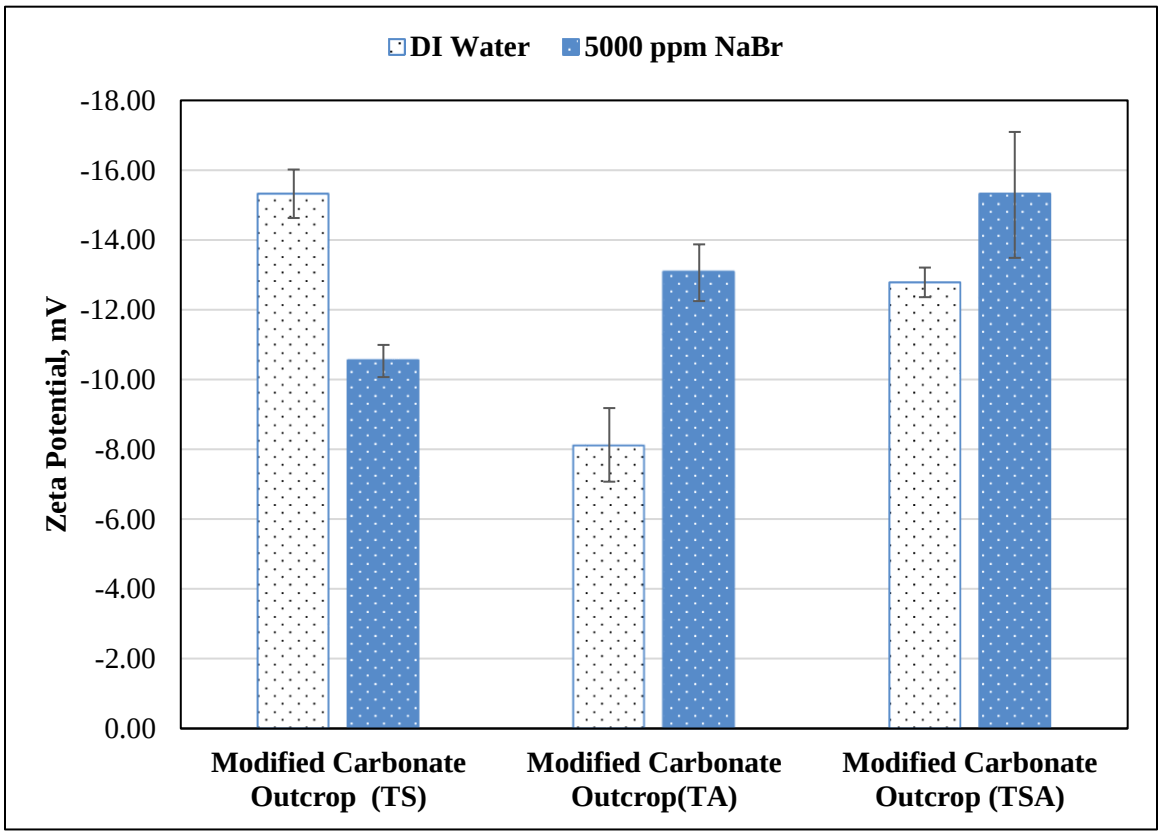

Figure 19: ζ values of modified carbonate rock particles suspended in DI water and in 5000 ppm NaBr at 7.5 pH and 25ºC

Figure 19 shows the ζ values of carbonate outcrop rock particles modified with model oils and then treated with 5000 ppm NaBr. It is observed that the ζ values of modified rocks (TA and TSA) are higher than the corresponding values in DI water, which is attributed to the adsorption of bromide ions on the rock surface that increased the magnitude of zeta

potential. The ζ value of modified rocks (TS) reduced as compared to the corresponding ζ value in DI water. It is most likely due to the release of adsorbed stearic acid from the rock surface, that lowered the ζ value.

On the basis of zeta potential measurements of modified carbonate outcrop treated with different low salinity brines, it is concluded that all brines (5000 ppm or NaCl, NaBr or NaI, respectively) are effective in modifying the rock wettability toward less oil wet in case of modified rock (TS). It was determined earlier in section 4.2 that conditioning of modified carbonate outcrop in DI water has already released asphaltene from the carbonate rock surface. Thus, conditioning of modified carbonate rock (TA and TSA) in low salinity brines (5000 ppm or NaCl, NaBr or NaI, respectively), increased the magnitude of zeta potential due to adsorption of respective anions on the rock surface.

By observing the zeta potential measurements of modified carbonate outcrop, it seems that low salinity brines are effective for only carbonate outcrop modified with model oil (TS), while DI water is effective for other modified carbonate outcrop (TA or TSA). To corroborate our observations from zeta potential measurements, we performed a simple floatation test in which we conditioned the carbonate outcrop particles in 5000 ppm NaI and in DI water. After conditioning, we checked either particles were floating or settling at the bottom. It is shown in Figure 20 that for modified rock (TS), we observe less floating particles when modified carbonate rock was conditioned in 5000 ppm NaI than in DI water. While, for carbonate rock modified with model oil (TA or TSA), conditioning in DI water is showing less floating particles than in 5000 ppm NaI. This observation is in complete agreement with our analysis of zeta potential measurements. On the basis of zeta potential measurements of modified carbonate outcrop treated with different brines, it is concluded

that all brines (5000 ppm NaBr, 5000 ppm NaCl and 5000 ppm NaI) are effective in modifying the rock wettability toward less oil wet in case of modified rock (TS). It was determined earlier in section 4.2 that conditioning of modified carbonate outcrop in DI water has already released asphaltene from the carbonate rock surface. Thus, conditioning of modified carbonate rock (TA and TSA) in 5000 ppm NaCl and in 5000 ppm NaBr only increased the magnitude of zeta potential due to adsorption of ions on the rock surface

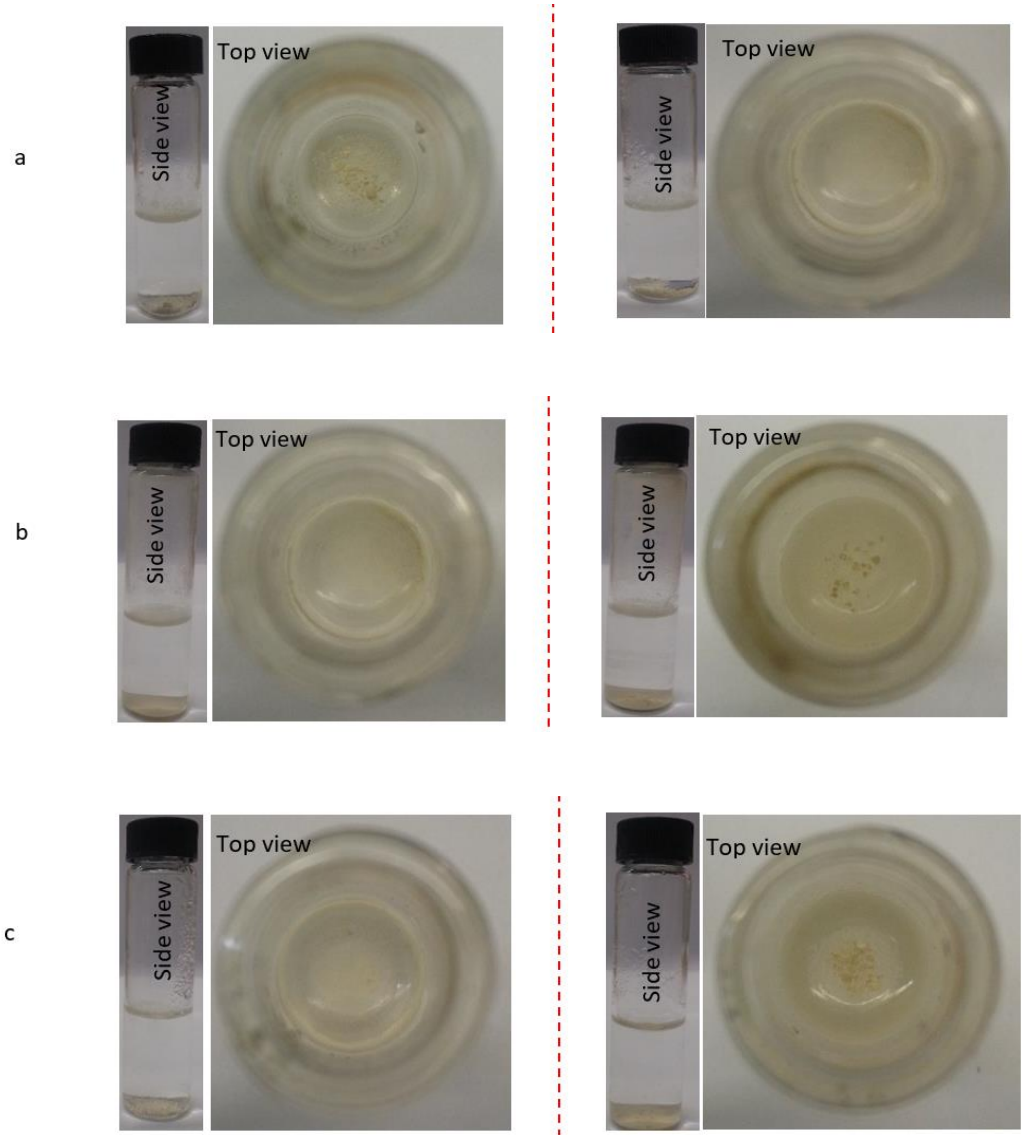

Figure 20 Floatation test of modified carbonate outcrop conditioned with (a) model oil (TS), (b) model oil (TA) and model oil (TSA) conditioned in DI water (left) and in 5000 ppm NaI (right)

4.10 Zeta potential of unmodified calcite treated in low salinity brines, dried and measured ζ in DI

Unmodified calcite particles were allowed to condition in a multi-wrist shaker for 24 hours at 25°C with different salt solutions (NaI. NaBr and NaCl) of 5000 ppm. After conditioning, all solutions were allowed to settle the course particle and supernatant was removed. Then supernatants were filtered by 0.5-micron filter paper to remove solid particles and all filtrates were analyzed by ICP-OES to find the composition of filtrate as presented in Table 8 and the residue solid particles were added to DI water in 0.5 wt. % solid to liquid ratio. Successive zeta potential measurements were conducted right after adding the particles in DI water and also 24 hours and 48 hours after the addition as shown in Figure 21.

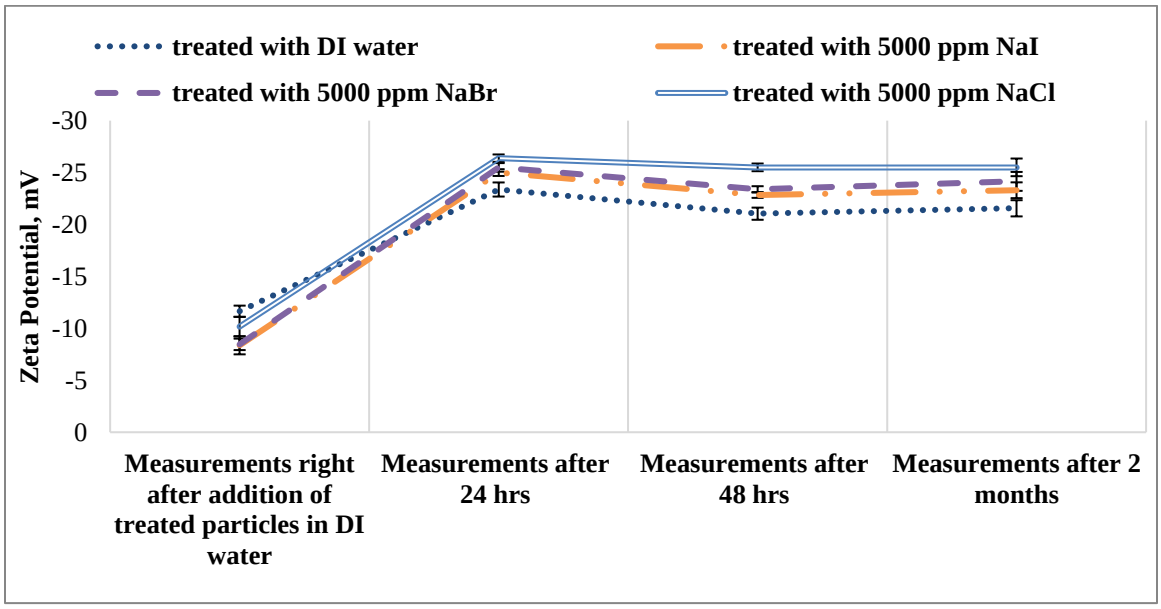

Figure 21: Unmodified calcite rock particles conditioned in DI water and different salt solutions for 24 hours, then filtered and the residue was incubated in deionized water for ζ measurements with time lapse at unadjusted pH and 25°C.

As shown in Figure 21, zeta potential measurements conducted immediately after adding treated particles in DI water show less negative ζ as compared to succeeding measurement after 24 hours. It can be seen from these results that after 24 hours, all zeta potential values are bot changing indicating that zeta potential reached equilibrium after 24 hours.

It is interesting to compare the ζ values of treated calcite rock particles (prior conditioned with respective salt solutions) in DI water as shown in Figure 21 and the ζ values of unmodified calcite particles measured in respective salt solutions, with unchanged pH. The comparison is shown in Table 10.

Table 10: Comparison of ζ values of prior treated calcite rock particles and untreated calcite particles in DI water

	ζ values of unmodified calcite particles measured in respective salt solutions, with unchanged pH	**ζ values of treated calcite rock particles (prior conditioned with respective salt solutions) in DI water, with unchanged pH**
DI water	-9.57±0.82 @ pH 9.42	-23.37±0.68 @ pH 8.96
NaI (I.S = 0.033M)	-12.76±0.2 @ pH 8.81	-25.00±0.33 @ pH 9.08
NaBr (I.S = 0.049M)	-10.51±1.5 @ pH 8.44	-25.50±0.41 @ pH 9.07
NaCl (I.S = 0.086M)	-10.88±0.53 @ pH 9.07	-26.39±0.36 @ pH 9.02

It is noted from Table 10 that when unmodified calcite particles conditioned in single salts solution, followed by drying and conditioning again in DI water, the calcite dissolution takes place again leading to more negative zeta potential.

It is also observed from Figure 21 that the magnitude of ζ values increased monotonically with respect to the molar concentration of the solutions. Since each salt solution has the

same mass (5 g of each salt in 1 kg water), NaCl holds the maximum number of moles as compared to the other two salt solution, while NaBr holds less number of moles than NaCl and NaI holds the least number of moles.

4.11 Zeta potential of unmodified calcite treated in high salinity brines, dried and measured ζ in DI

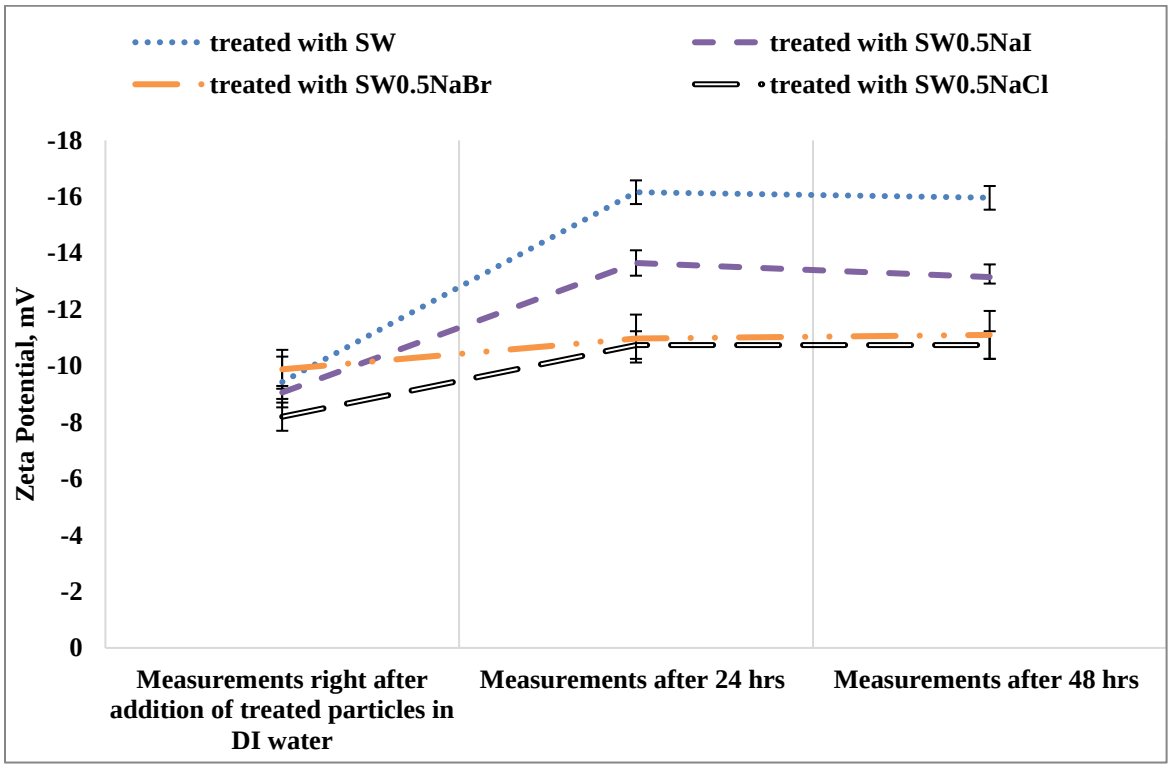

Figure 22: Unmodified calcite rock particles conditioned in DI water and different salt solutions (SW, SW0.5NaI, SW0.5NaBr & SW0.5 NaCl) for 24 hours, then filtered and the residue was incubated in deionized water for ζ measurements with time lapse at 25°C.

It is observed from Figure 22 that calcite rock particles that are prior treated with salt solutions of high salinity, when incubated in DI water, the dissolution is as significant as it was observed with low salinity brines.

4.12 Zeta potential of unmodified calcite and carbonate outcrop particles conditioned in high salinity brines

Unmodified calcite particles conditioned in sea water (SW) shows positive zeta potential value while carbonate outcrop shows negative zeta potential value as shown in Figure 23. The surface charge of calcite in sea water is positive as reported in several studies. Mahani et al. [111] reported ζ of 0.2 mV for calcite in sea water (salinity~44, 000 ppm) at pH 7.5 while Shehata et al. [128] reported ζ of +12.9 mV for calcite in sea water (salinity~55,000 ppm) at pH 7.8. The large variation in the reported values is due to the variation in the composition of sea water and brine salinity used in their studies. However, in all studies, the charge on calcite in sea water is positive.

The ζ potential of carbonate outcrop in sea water is negative (-6.83±1.08 mV). Many studies were carried out on carbonate rock conditioned in sea water. The results are in agreement with the reported studies. Al-Quraishi [131] reported ζ of -1.5 mV for carbonate rock in sea water (salinity~68,000 ppm) while Mahani et al. [33] reported ζ of -5 mV for carbonate rock in sea water (salinity~44,000 ppm). In this study, the magnitude of zeta potential of carbonate outcrop is higher than the magnitude of calcite for all used brines in this study. This observation is in agreement with the results reported by Chen et al. [80].

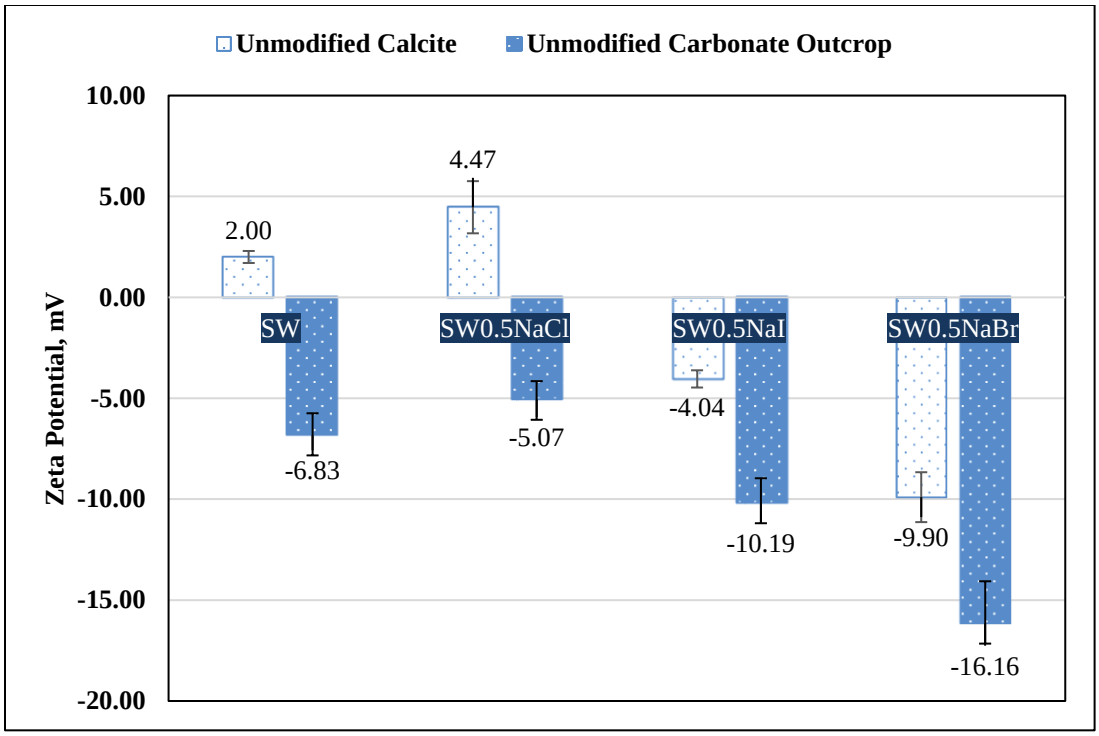

Figure 23: ζ of unmodified calcite and carbonate outcrop rock particles suspended in different salt solutions (SW, SW0.5NaI, SW0.5NaCl, SW0.5NaBr) at 7.5 pH at 25ºC.

It is observed that the magnitude of negative zeta potential increased in brines, that were in contact with the rocks (calcite and carbonate outcrop), in the sequence SW0.5NaCl < SW0.5NaI < SW0.5NaBr. The same trend was also observed while using the unmodified rocks with low salinity brines (containing 5000 ppm of NaCl, NaI and NaBr, respectively) as shown in Figure 12. It is observed from Figure 23 that the zeta potential of unmodified calcite and carbonate outcrop particles conditioned in SW0.5NaCl is higher than the corresponding values in sea water (SW). One explanation of this is that the addition of 0.5 wt.% NaCl in sea water (i.e. SW0.5NaCl) restrained the interaction of potential determining ion (SO_4^{2-}) with the rock surface and that, consequently, reduced the overall negative charge around the particle. A similar observation was observed by Fathi et al.[70] during spontaneous imbibition experiments that the removal of NaCl from sea water

composition increased the oil recovery. They reported that if the concentration of Cl^- ions in the sea water increase, SO_4^{2-} ions could not have a better access to the surface of rock.

In case of conditioning of both rocks in SW and in SW0.5NaCl, the zeta potential measurements showed positive values (+2.00±0.29 mV in SW and +4.47±1.29 mV in SW0.5NaCl) for calcite rock and negative values (-6.83±0.95 mV in SW and -5.07±0.91 mV in SW0.5NaCl) for carbonate outcrop rock. It is determined from XRD and XRF results of both rocks that calcite is pure calcium carbonate ($CaCO_3$) while carbonate outcrop have some amount of silica that exhibits negative charge around the particles and this could be the reason of negative ζ value on carbonate surface and positive charge on calcite surface conditioned in SW and SW0.5NaCl. It is observed that SW0.5NaBr and SW0.5NaI increased the negative charge on both rocks as compared to the charge present when rocks were conditioned in SW. It was determined earlier that iodide and bromide ions absorbs on the rock surface and due to the adsorption of these ions, the zeta potential becomes more negative. The results of both rocks conditioned in SW0.5NaBr and SW0.5NaI also shows that the zeta potential becomes more negative due to the adsorption of iodide and bromide ions on the rock surface.

4.13 Zeta potential of calcite particles modified with model oils and conditioned in SW0.5NaCl and in SW.

Calcite rock particles modified with model oils show negative charge in sea water (SW) as shown in Figure 24. It is attributed that the adsorbed oil component from the model oil shifted the zeta potential to negative as compared to the zeta potential of unmodified calcite in sea water, which showed positive zeta potential value (+2±0.29 mV) as shown in Figure 23. The addition of 0.5 wt.% NaCl in sea water (SW0.5NaCl) further enhanced the negative

charge of modified calcite (TS, TA and TSA) as compared to the corresponding values of modified rock particles in SW as shown in Figure 24. It is attributed to the increase of negative charges around the rock particle due to the accumulation of Cl^- ions in the diffuse layer. Consequently, the magnitude of negative zeta potential value is increased. Fathi et al. [70] also observed that NaCl acts as non-active salts in sea water and the presence of large amount of NaCl in sea water resist the access of active ions (SO_4^{2-}) onto the rock. They observed a reduction in oil recovery when NaCl concentration in sea water was increased.

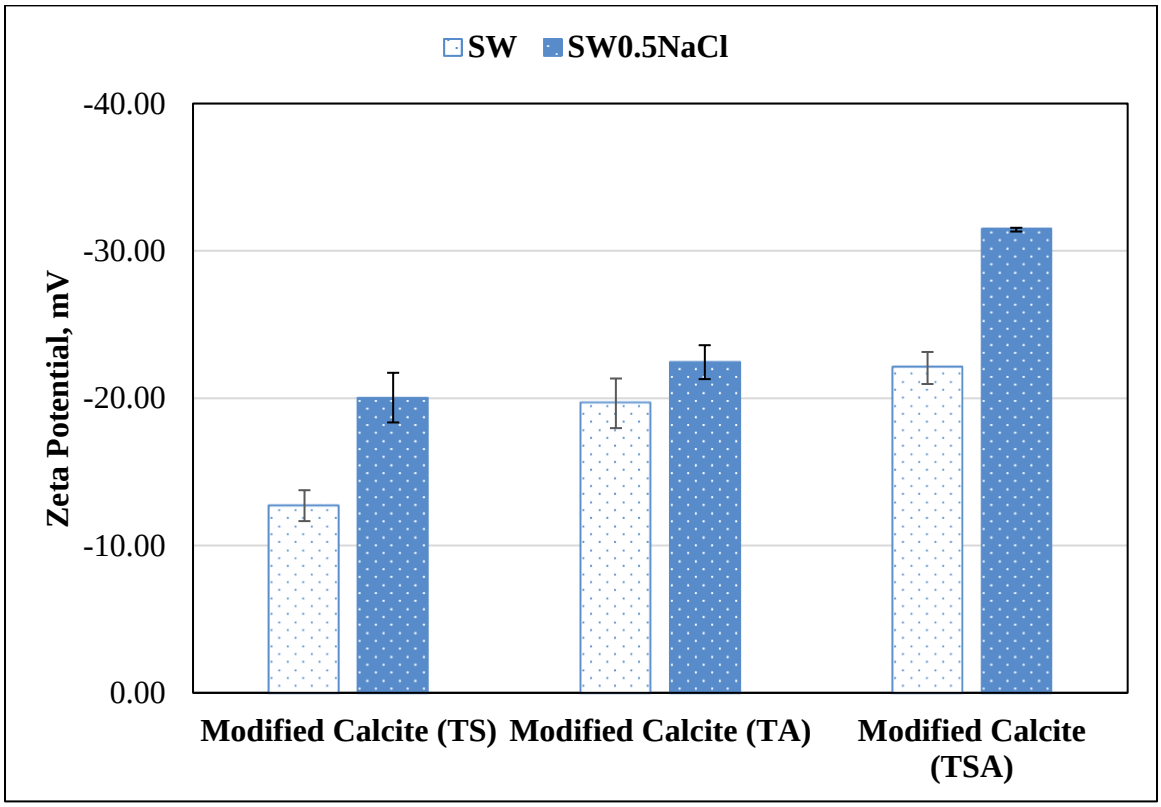

Figure 24: Zeta potential of calcite modified with model oil (TS) and then conditioned in SW, SW0.5NaCl, SW0.5NaI and SW0.5NaBr.

4.14 Zeta potential of carbonate outcrop particles modified with model oils and then conditioned in SW0.5NaCl and in SW.

Figure 25 shows the zeta potential of carbonate outcrop modified with model oils and then conditioned in SW0.5NaCl. It shows similar behavior as observed with calcite particles modified with model oil and then conditioned in SW0.5NaCl, Figure 24. Carbonate outcrop rock particles modified with model oil (TS) shows negative charge in sea water (SW) as shown in Figure 25. It is attributed that the adsorbed oil components from the model oils increase the negative charge as compared to the zeta potential of unmodified carbonate outcrop in sea water (-6.83±0.95 mV), as shown in Figure 23. The addition of 0.5 wt.% NaCl in sea water (SW0.5NaCl) further enhanced the negative charge of modified carbonate outcrop up to -28.84±1.54 mV. It is attributed to the increase of negative charges around the rock particle due to the accumulation of Cl^- ions in the diffuse layer. Consequently, the magnitude of negative zeta potential value is increased. Fathi et al. [70] also observed the inactive role of NaCl in sea water and the presence of NaCl in sea water resisted the access of active ions (SO_4^{2-}) onto the rock. They observed a reduction in oil recovery when NaCl concentration in sea water was increased.

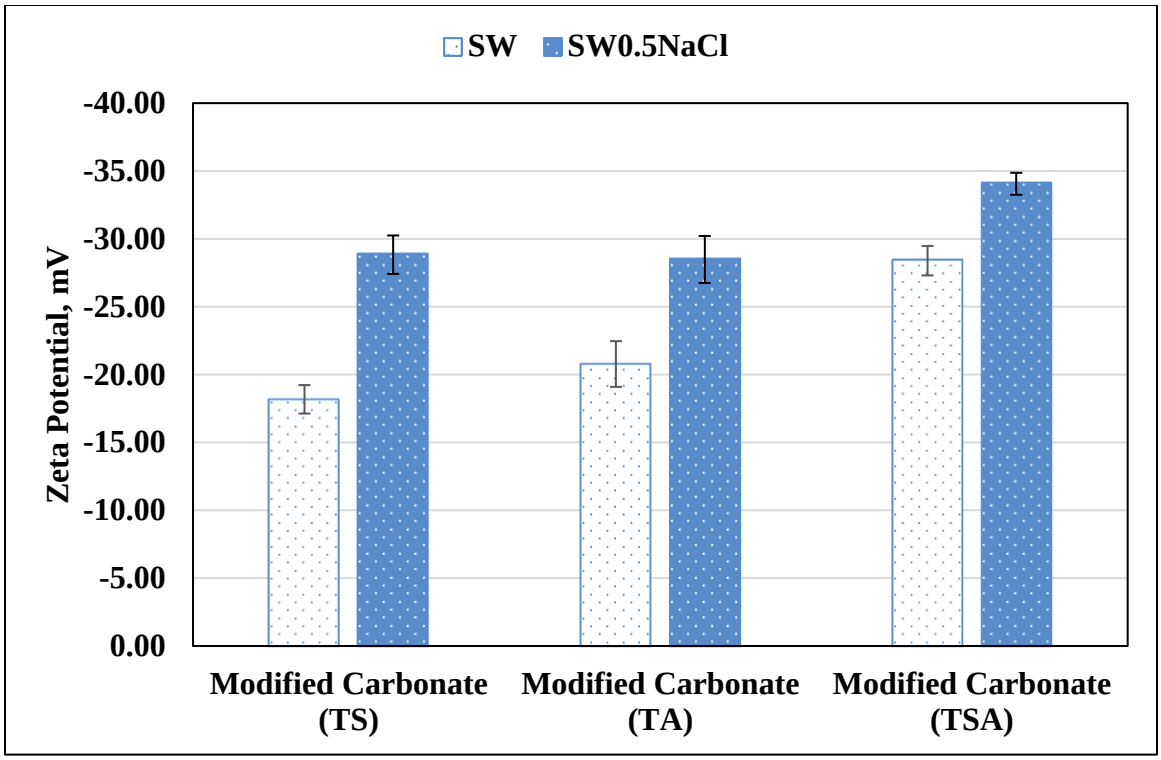

Figure 25: Zeta potential of carbonate outcrop modified with model oil (TS)

4.15 Zeta potential of calcite particles modified with model oils and then conditioned in SW0.5NaI and in SW.

Figure 26 shows the zeta potential of calcite modified with model oils and conditioned in SW0.5NaI. It is interesting to note that the addition of 5000 ppm NaI in sea water (SW0.5NaI) reduced the negative charge from the rock surface and showed the lowest negative zeta potential values as compared to all other modified calcite rock conditioned in high salinity brines. The decrease of the negative charges is attributed to the release of polar oil components from the rock surface. Thus, SW0.5NaI shows high potential in altering the surface rock properties and releasing the adsorbed polar oil components from the rock surfaces.

Comparison of all high salinity brines shows that the minimum negative zeta potential is observed with modified calcite rocks conditioned in SW0.5NaI as compared to SW,

SW0.5NaBr and SW0.5NaCl. This observation is in line with the zeta potential results of modified calcite rock conditioned in low salinity brines, which shows that 5000 ppm NaI is the most effective brine than 5000 ppm NaBr and 5000 ppm NaCl. It shows that 5000 ppm NaI and SW0.5NaI have a positive effect on altering the calcite rock wettability toward less oil wet.

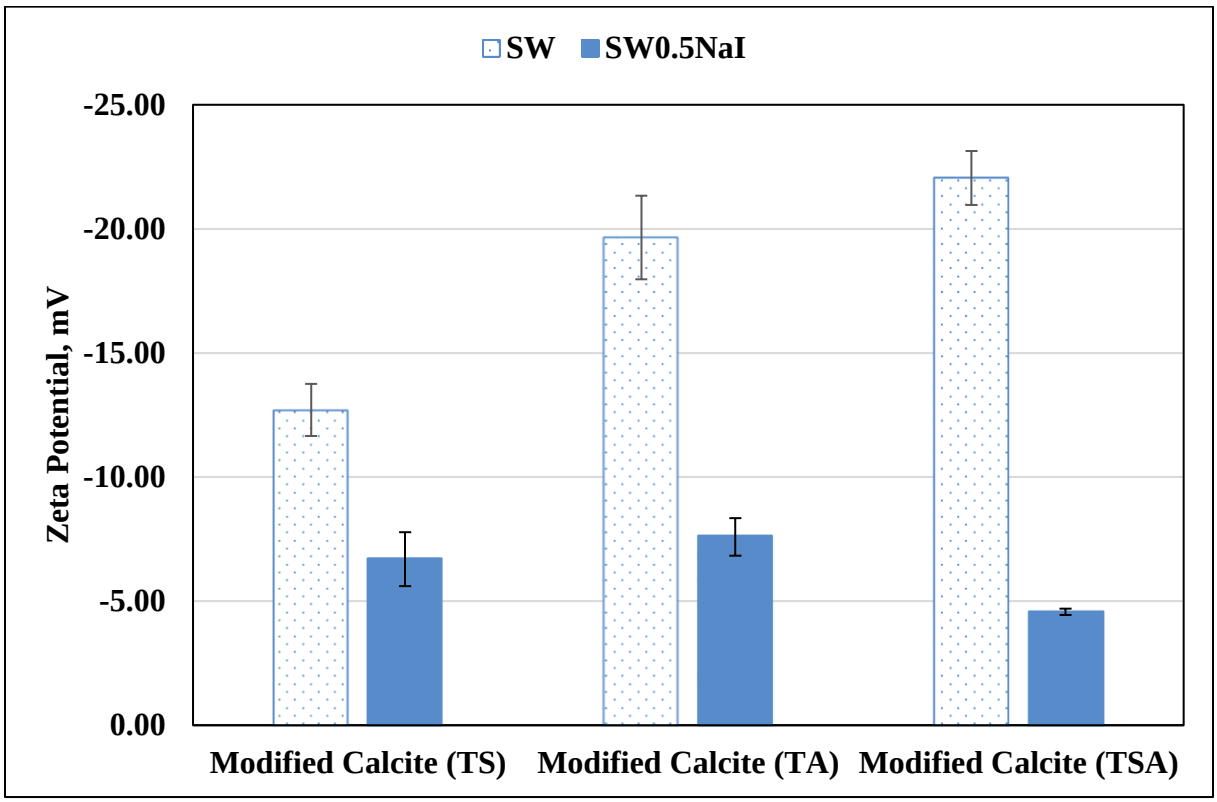

Figure 26: Zeta potential of calcite modified with model oil (TA)

4.16 Zeta potential of carbonate outcrop particles modified with model oils and then conditioned in SW0.5NaI and in SW.

Figure 27 shows the zeta potential of carbonate outcrop modified with model oils and conditioned in SW0.5NaI. Interestingly, the addition of 5000 ppm NaI in sea water (SW0.5NaI) reduced the negative charge from the rock surface and showed the minimum negative zeta potential as compared to all other modified rock conditioned in high salinity

brines. The decrease of negative charge is attributed to the release of polar oil components from the rock surface. Thus, SW0.5NaI shows high potential in altering the surface rock properties and releasing the adsorbed polar oil components from the rock surfaces.

Comparison of all high salinity brines shows that the minimum negative zeta potential is observed with modified carbonate outcrop rocks conditioned in SW0.5NaI as compared to modified carbonate outcrop rocks conditioned in SW, SW0.5NaBr and SW0.5NaCl. No correlation was observed with the results of zeta potential of modified carbonate outcrop rocks conditioned in low salinity brines (500 ppm NaCl, 5000 ppm NaBr and 5000 ppm NaI).

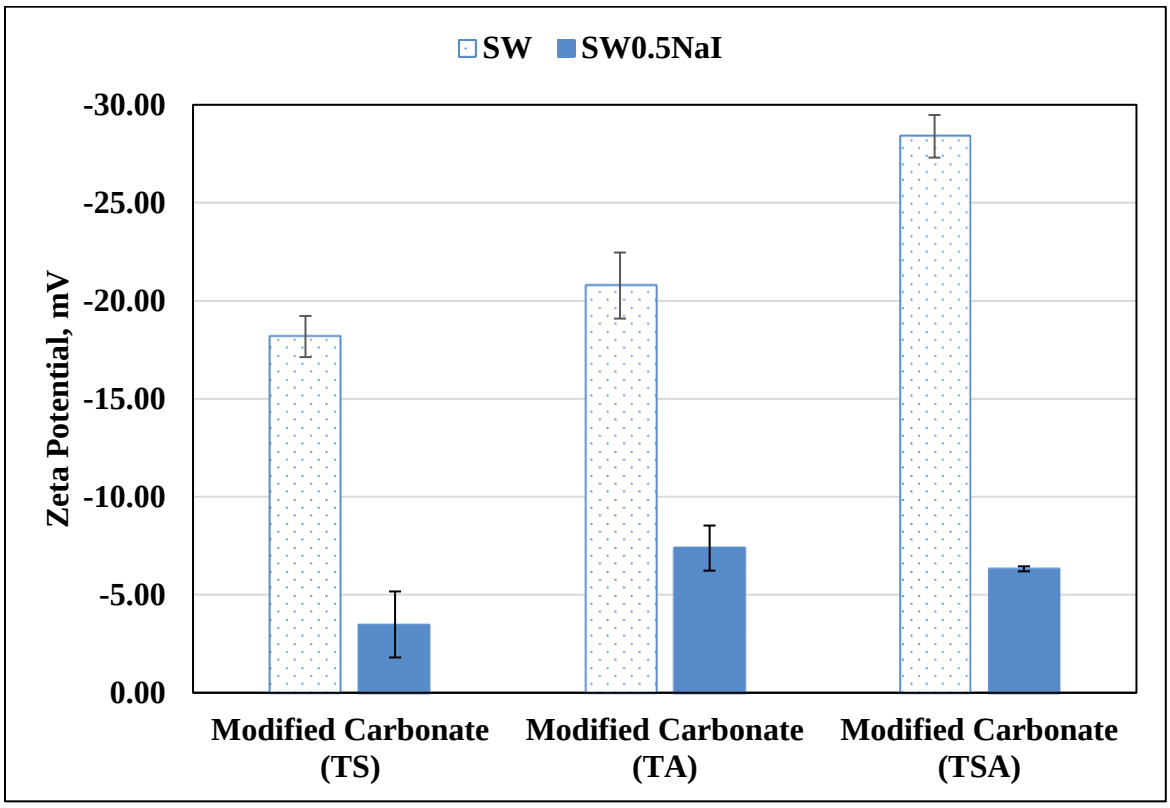

Figure 27: Zeta potential of carbonate outcrop modified with model oil (TA)

4.17 Zeta potential of calcite particles modified with model oils and conditioned in SW0.5NaBr and in SW.

Figure 28 shows the effect of calcite rock particles modified with model oils and then conditioned in SW0.5NaBr. It is observed that the magnitude of zeta potential reduced when modified rock particles were conditioned with SW0.5NaBr as compared to the corresponding value in SW. It is attributed to the release of adsorbed oil components from the rock surface. This response is similar to the zeta potential response of modified calcite rock conditioned in SW0.5NaI. However, in term of zeta potential magnitude, the effect of SW0.5NaBr is not significant as SW0.5NaI.

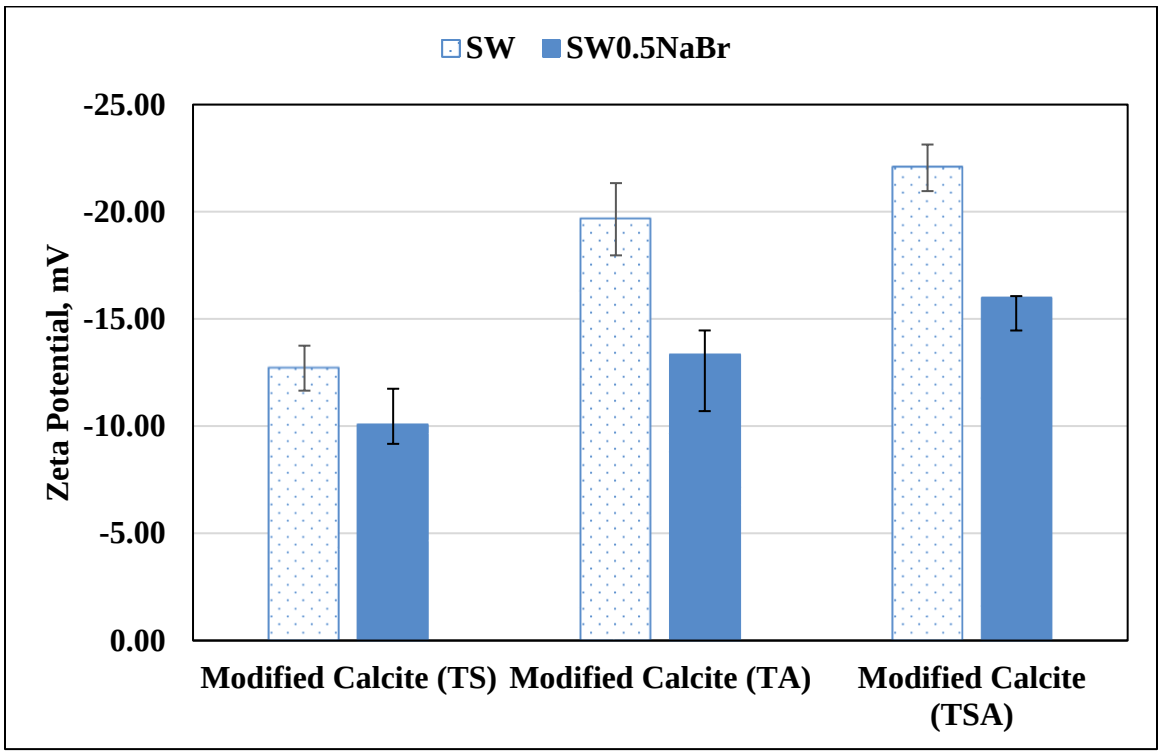

Figure 28: Zeta potential of calcite modified with model oil (TSA)

4.18 Zeta potential of carbonate outcrop particles modified with model oil (TSA) and conditioned in SW0.5NaBr and in SW

Figure 29 shows the effect of carbonate outcrop modified with model oils and conditioned in SW0.5NaBr. It is observed that the magnitude of zeta potential was reduced when modified rock particles were conditioned with SW0.5NaBr as compared to the corresponding values in SW. It is attributed to the release of adsorbed oil components from the rock surface. This response is similar to the zeta potential response of modified calcite rock conditioned in SW0.5NaI. However, in term of zeta potential magnitude, the effect of SW0.5NaBr is not as significant as SW0.5NaI.

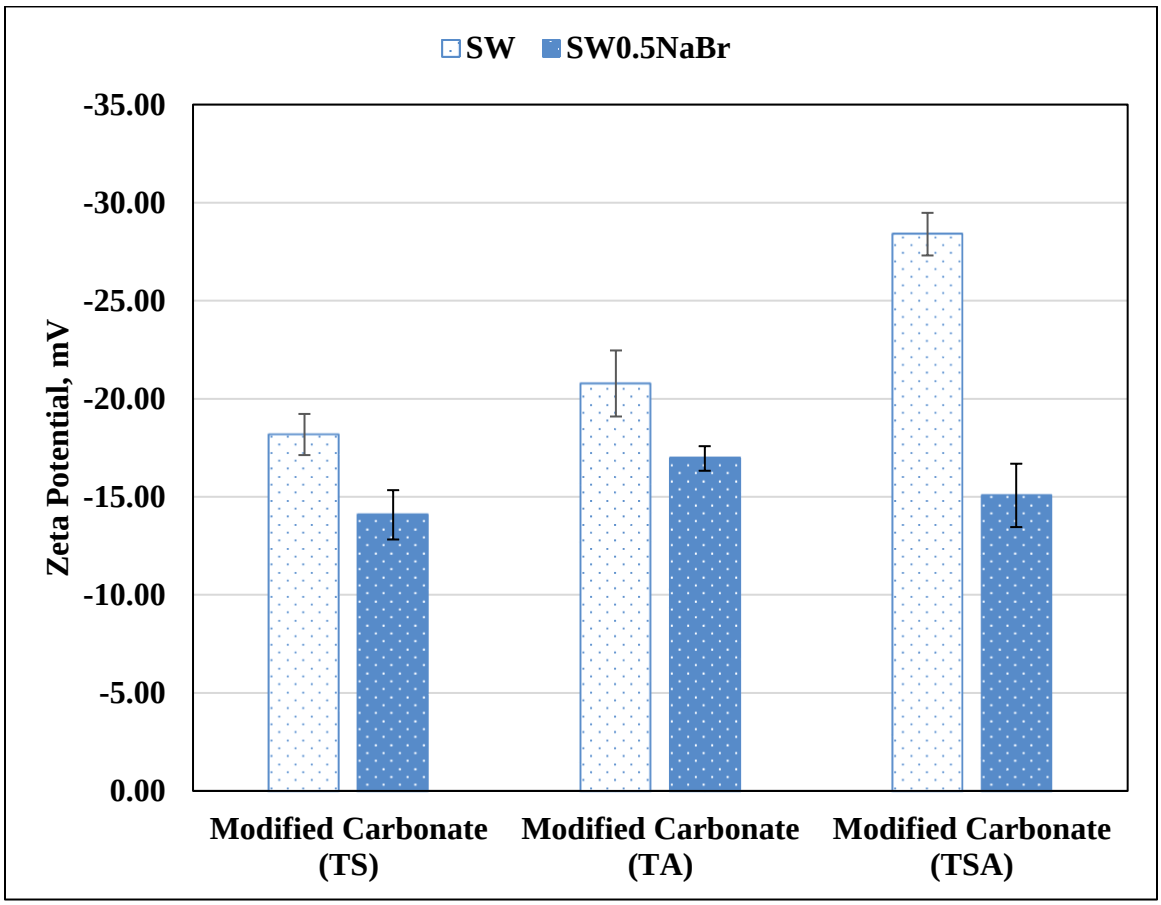

Figure 29: Zeta potential of carbonate outcrop modified with model oil (TSA)

4.19 Surface characterization of unmodified calcite using SEM-EDS

Calcite rock particles were analyzed by SEM-EDS to identify the constituent elements of the rock and to measure the elemental composition as shown in Figure 30. Only three elements were detected from the EDS spectra of calcite that were calcium, oxygen and carbon which indicates that the calcite rock used in this study was pure calcium carbonate ($CaCO_3$). The present results also confirmed the results obtained by XRD that showed pure $CaCO_3$ mineral. Table 11 summarizes the results of EDS spectra. Among all elements, calcium concentration was highest for all observed sites.

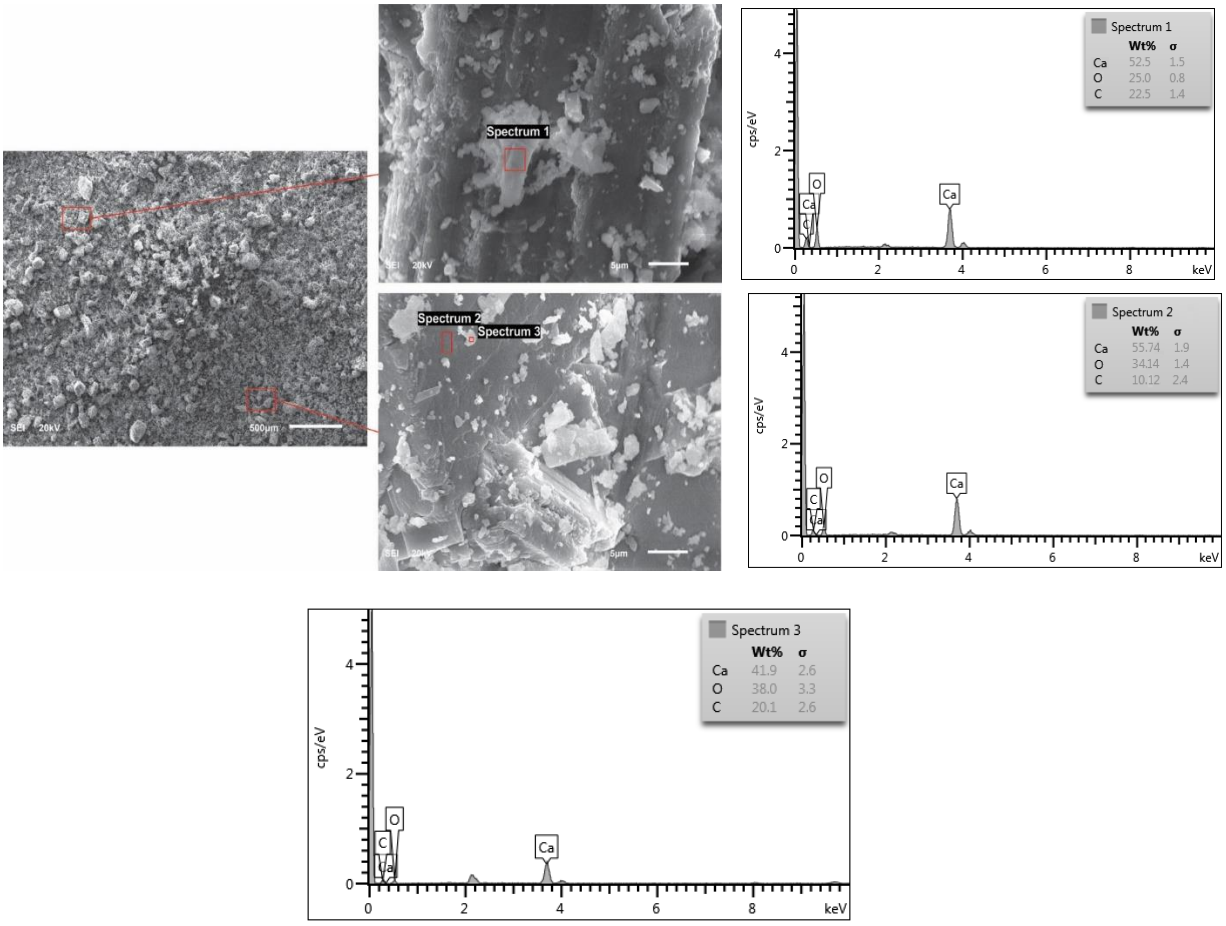

Figure 30: SEM image (top left) and EDS spectra (top right & bottom) of the unmodified calcite

Table 11: Elemental composition for different spots as highlight in SEM image of calcite

Element	Spectrum 1	Spectrum 2	Spectrum 3
C	22.54	10.12	20.12
O	24.96	34.14	37.96
Ca	52.50	55.74	41.92
Total:	100.0	100.00	100.00

Table 12: Comparison of observed elemental composition with literature

Element	Average of three spectrums (this study)	Karimi et al. [132]	Ahmed Kasha [100]
C	17.59	17.1	15
O	32.35	35.5	43
Ca	50.05	47.5	42
Total:	100.0	100.00	100.00

It is interesting to note that the results obtained by EDS are consistent with the results reported in the literature. Table 12 compares the average elemental composition of all spectrum obtained by this study with the composition provided in the literature from different sources.

4.20 Surface characterization of modified calcite with model oil (TS) using SEM-EDS

Calcite rock particles modified with model oil (TS) were analyzed by SEM-EDS to validate the adsorption of stearic acid on the rock surface. Figure 31 shows the SEM-EDS spectra of the adsorbed rock particles while Table 13 summarizes the elemental composition of the SEM-EDS spectra. Comparing the results of unmodified calcite particles (Carbon~17.59%, Oxygen~32.35% and Calcium~50.05%) and calcite rock particles modified with model oil (TS) (Carbon~19.10%, Oxygen~48.95% and calcium~31.95%), it is observed that modified calcite particles show comparatively less calcium concentration and high carbon and oxygen concentration. It is attributed to the adsorption of stearic acid on the calcite surface. Stearic acid contains carboxylate (~$COOH^-$) ion that has the capability to adsorb on the rock particle [133]. The adsorption of carboxylate ion on the calcite surface increases the concentrations of carbon and oxygen while comparatively, the concentration of calcium reduces. In another study on pure calcite rock, Karimi et al. [132] also observed that when stearic acid is adsorbed on calcite surface, the adsorption of stearate increase concentrations of oxygen and carbon, while reduce the concentration of calcium.

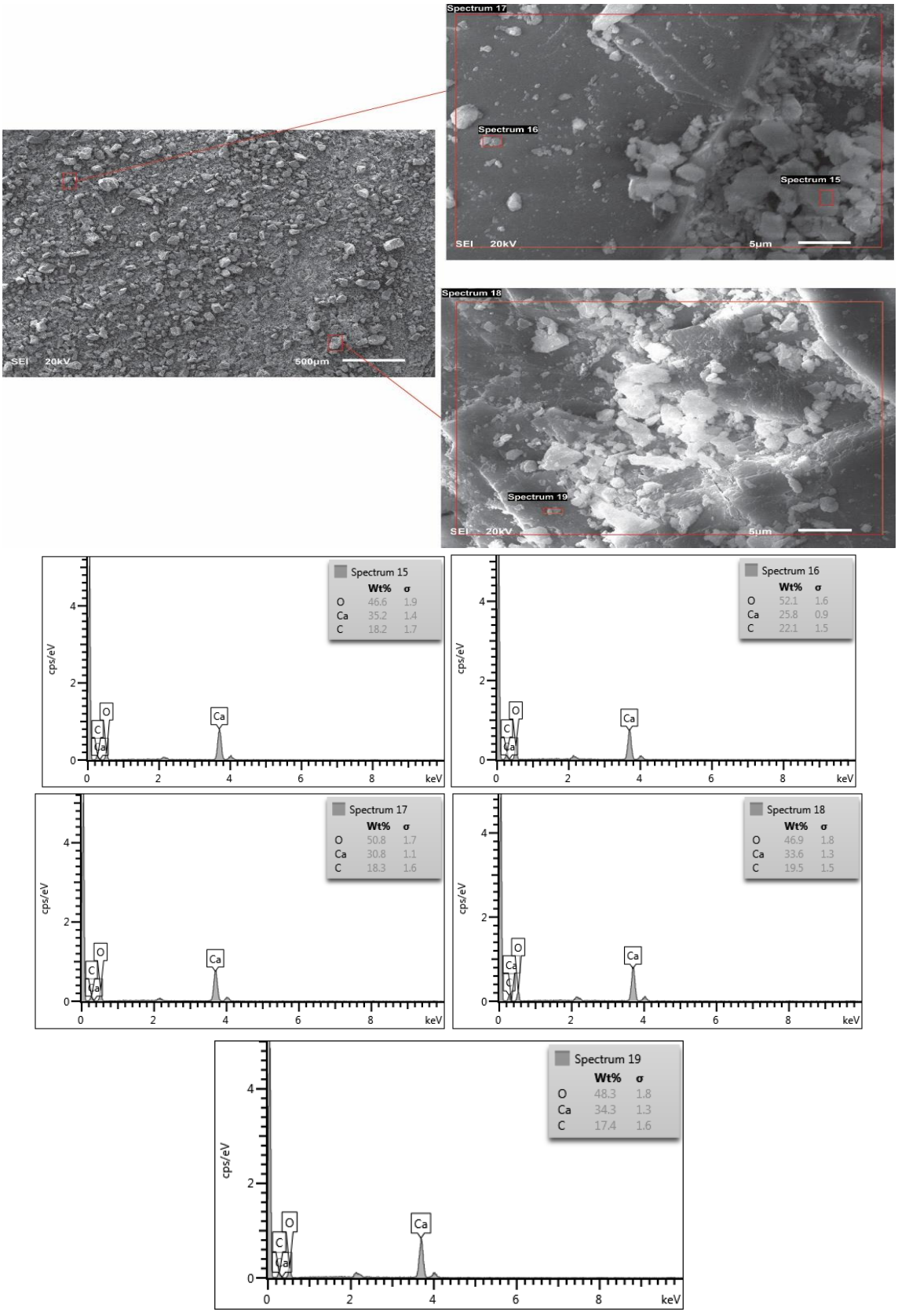

Figure 31: SEM image (top) and EDS spectra (bottom) of calcite modified with model oil(TS)

Table 13: Elemental composition for different spots as highlighted in SEM image of modified calcite (TS)

Element	Spectrum 15	Spectrum 16	Spectrum 17	Spectrum 18	Spectrum 19
C	18.20	22.13	18.30	19.46	17.43
O	46.62	52.09	50.85	46.91	48.28
Ca	35.19	25.78	30.85	33.63	34.29
Total:	100.00	100.00	100.00	100.00	100.00

Table 14 shows the comparison of our results with the reported results in the literature. Our results match perfectly with Karimi et al. [132] while as compared to Kasha [100], they are completely off. However, one thing is common in all that the calcium concentration decreases when rock adsorb stearic acid. Thus, instead of comparing carbon and oxygen concentrations to identify whether rock adsorb oil or not, we can compare concentration of only one element that is calcium. From the analysis of unmodified and modified calcite rock, we can define a cutoff point that if the concentration of calcite is equal to or greater than 40% [which is the average calcium concentration of unmodified and modified calcite (TS)], it can be treated as pure calcite while if calcium concentration is below 40%, it can be considered as an adsorbed surface with stearic acid.

Table 14: Comparison of observed elemental composition with literature

Element	Average of five spectrums (this study)	Karimi et al. [132]	Ahmed Kasha [100]
C	19.104	19.4	58.43
O	48.95	48.2	23.13
Ca	31.948	32.3	18.43
Total:	100.00	100.00	100.00

4.21 Surface characterization of unmodified carbonate outcrop using SEM-EDS

Carbonate outcrop particles were analyzed by SEM-EDS to identify the constituent elements of the rock and to measure the elemental composition as shown in Figure 32. EDS spectra detects calcium, carbon and oxygen which indicates calcium carbonate ($CaCO_3$). However, the percentage of calcium is highest as shown in Table 15. Small percentage of silicon can also be seen which indicates the presence of SiO_2. These results verify the results obtained by XRD.

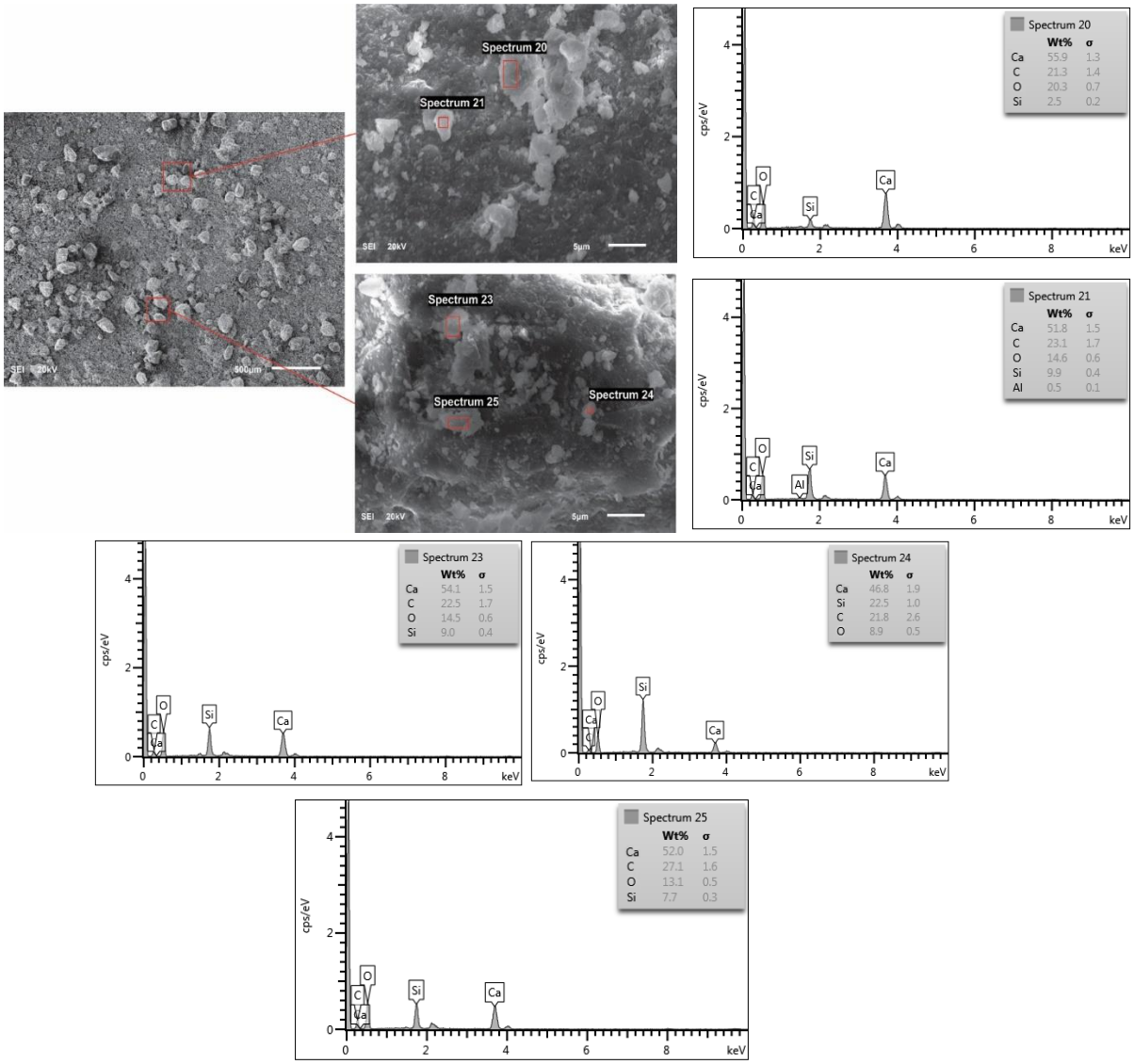

Figure 32: SEM image (top left) and EDS spectra (top right & bottom) of unmodified carbonate outcrop

Table 15: Elemental composition for different spots as highlighted in SEM image of unmodified carbonate outcrop

Element	Spectrum 20	Spectrum 21	Spectrum 23	Spectrum 24	Spectrum 25
C	21.34	23.24	22.46	21.85	27.15
O	20.27	14.74	14.47	8.87	13.14
Si	2.51	10.01	9.00	22.49	7.67
Ca	55.88	51.89	54.07	46.80	52.04
Total:	100.00	100.00	100.00	100.00	100.00

4.22 Surface characterization of modified carbonate outcrop with model oil (TS) using SEM-EDS

Carbonate outcrop particles modified with model oil (TS) is shown in Figure 33 and Table 16 summarizes the elemental composition obtained by EDS spectra. If we examine the composition of unmodified and modified carbonate rock particles with our cutoff point of 40% calcium concentration, we can say that the stearic acid is adsorbed on the carbonate rock outcrop on observed sites. There was an increase in concentrations of oxygen and carbon percentage while calcium concentration reduced as compared to unmodified carbonate rock outcrop. Moreover, the concentration of silicon is reduced or almost zero on observed sites. It is possible that the carboxylic acid adsorbs on the calcium sites, which was relatively very high in concentration as compared to silica content. Thus, because of the minimal concentration of silica, the carboxylic group covered the calcium sites and also covered silica from detection in EDS.

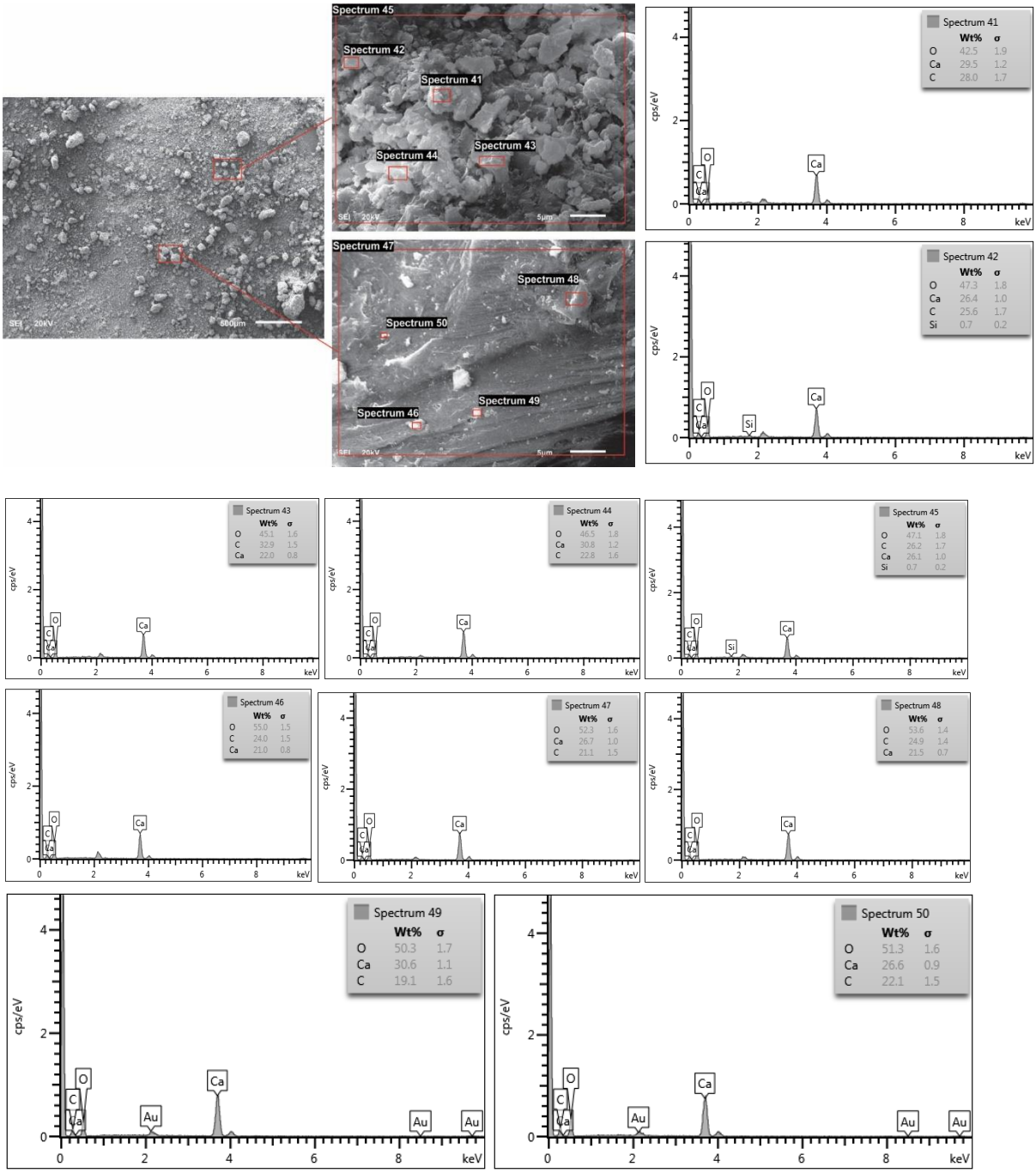

Figure 33: SEM image (top left) and EDS spectra (top right & bottom) of carbonate outcrop modified with model oil (TS)

Table 16: Elemental composition for different spots as highlighted in SEM image of modified carbonate outcrop with model oil (TS)

Element	Spectrum 41	Spectrum 42	Spectrum 43	Spectrum 44	Spectrum 45	Spectrum 46	Spectrum 47	Spectrum 48	Spectrum 49	Spectrum 50
C	28.00	25.56	32.89	22.76	26.15	24.00	21.09	24.85	19.13	22.15
O	42.55	47.33	45.09	46.47	47.10	55.04	52.26	53.61	50.27	51.29
Si	0.00	0.66	0.00	0.00	0.67	0.00	0.00	0.00	0.00	0.00
Ca	29.45	26.45	22.02	30.77	26.08	20.96	26.65	21.53	30.60	26.56
Total:	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

4.23 Surface characterization of modified calcite with model oil (TS) and treated in SW using SEM-EDS

Calcite rock particles modified with model oil (TS) and treated in SW is shown in Figure 34 and Table 17 summarizes the elemental composition obtained by EDS spectra. Surface changes can be observed from the SEM images. Some precipitation can also be seen on the surfaces. However, the results did not show any adsorption of Mg^{2+} and SO_4^{2-} ions that were present in the sea water. Karimi et al. [132] studied the interaction of sodium sulphate by treating a calcite rock modified with stearic and conditioned in sodium sulphate solution. They did not observe any traces of SO_4^{2-} ion adsorption on the calcite surface from EDS as well as FTIR spectra. So, we can rule out the multi-ion exchange mechanism during smart water flooding

Some sites show removal of stearic acid as it can be observed by comparing the concentration of ions. It is observed that spectrum 36, 37 and 38 show high concentration of calcium as compared to spectrum 35 and 39 while spectrum 40 shows the intermediate values, while carbon and oxygen concentrations show the reverse trend. Considering that the adsorption of stearic acid increases the concentration of carbon and oxygen and reduces calcium concentration. This shows that spectrum 35 and 39 are still oil wet whereas spectrum 36, 37, 38 and 40 are water wet. Thus, it can be concluded that treatment of oil

wet calcite with sea water partially release some oil components and alter the rock wettability to a more water-wet condition.

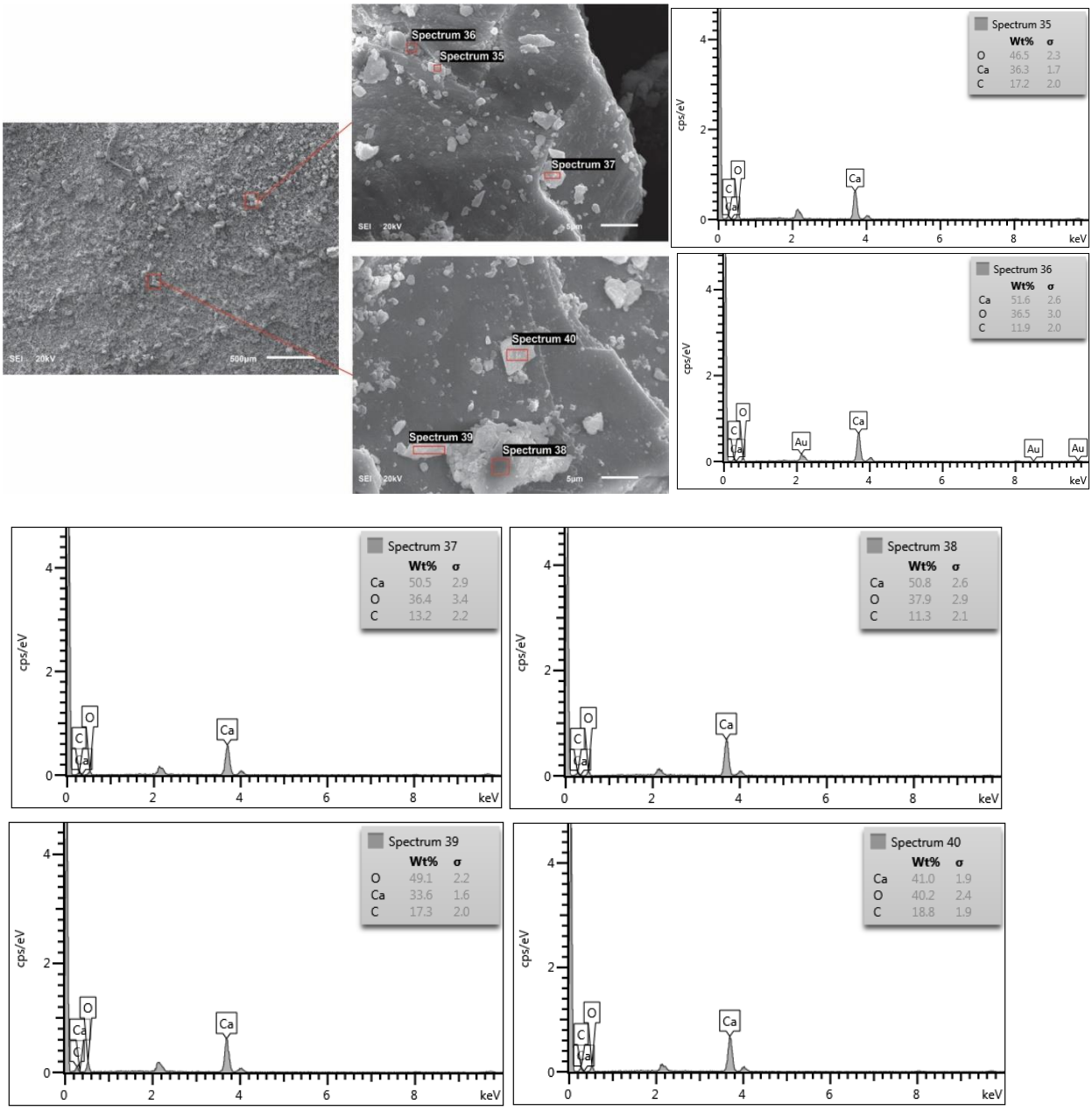

Figure 34: SEM image (top left) and EDS spectra (top right & bottom) of modified calcite rock with model oil (TS) and treated with sea water

Table 17: Elemental composition for different spots as highlighted in SEM image of modified calcite rock (TS) treated with SW

Element	Spectrum 35	Spectrum 36	Spectrum 37	Spectrum 38	Spectrum 39	Spectrum 40
C	17.21	11.88	13.16	11.33	17.30	18.82
O	46.52	36.49	36.39	37.91	49.13	40.21
Ca	36.27	51.62	50.46	50.76	33.57	40.97
Total:	100.00	100.00	100.00	100.00	100.00	100.00

4.24 Surface characterization of modified calcite with model oil (TS) and treated in SW0.5NaCl using SEM-EDS

Calcite rock particles modified with model oil (TS) and treated in SW0.5NaCl is shown in Figure 35 and Table 18 summarizes the elemental composition obtained by EDS spectra. It is observed that many sites (such as spectrum 27, 28 ,30, 31, 32 and 33) did not show good response and the interaction of SW0.5NaCl with modified calcite rock did not release stearic acid from the modified calcite rock surface. It can be determined by noticing the increase in concentrations of carbon and oxygen whereas decrease in concentration of calcium with respect to pure calcite. Moreover, few sites like spectrum 29 and spectrum 34 showed higher concentration of calcium which indicates water wet surface. There could be two possible reasons for that. Either SW0.5NaCl released some stearic acid or the other possibility is that those specific areas did not initially adsorb stearic acid. However, there are many sites showing adsorbed stearic acid on the surface and this confirms our previous statement that NaCl is present as a non-active salt in the sea water and the addition of NaCl in sea water does not release adsorbed polar oil components from the rock surface.

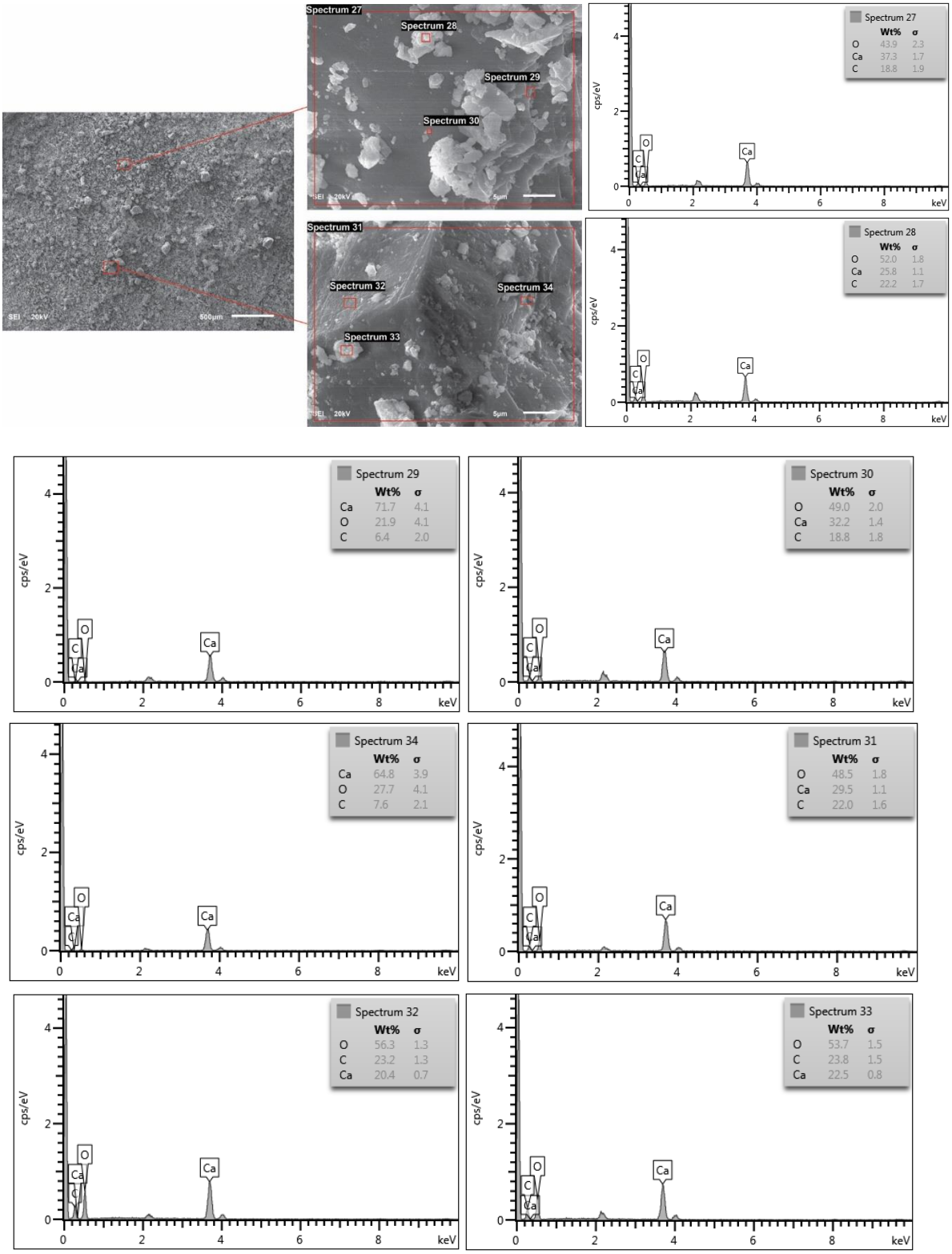

Figure 35: SEM image (top) and EDS spectra (bottom) of modified calcite rock with model oil (TS) and treated with SW0.5NaCl

Table 18: Elemental composition for different spots as highlighted in SEM image of modified calcite rock (TS) treated with SW0.5NaCl

Element	Spectrum 27	Spectrum 28	Spectrum 29	Spectrum 30	Spectrum 31	Spectrum 32	Spectrum 33	Spectrum 34
C	18.81	22.21	6.38	18.82	21.99	23.22	23.80	7.57
O	43.91	51.96	21.91	49.00	48.54	56.34	53.71	27.66
Ca	37.28	25.83	71.72	32.18	29.48	20.44	22.49	64.77
Total:	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

4.25 Surface characterization of modified calcite with model oil (TS) and treated in SW0.5NaBr using SEM-EDS

Figure 36 shows the SEM-EDS spectra of calcite rock particles modified with model oil (TS) and treated in SW0.5NaBr and Table 19 summarizes the elemental composition obtained by EDS spectra. It is observed that the addition of NaBr partially remove some stearic acid. As we discussed earlier that if calcium content is above 40 percent, the observed surface is pure calcite. Thus, spectrum 4, 7, 8 and 9 show adsorbed species on the surface while spectrum 5 and 6 show pure calcite.

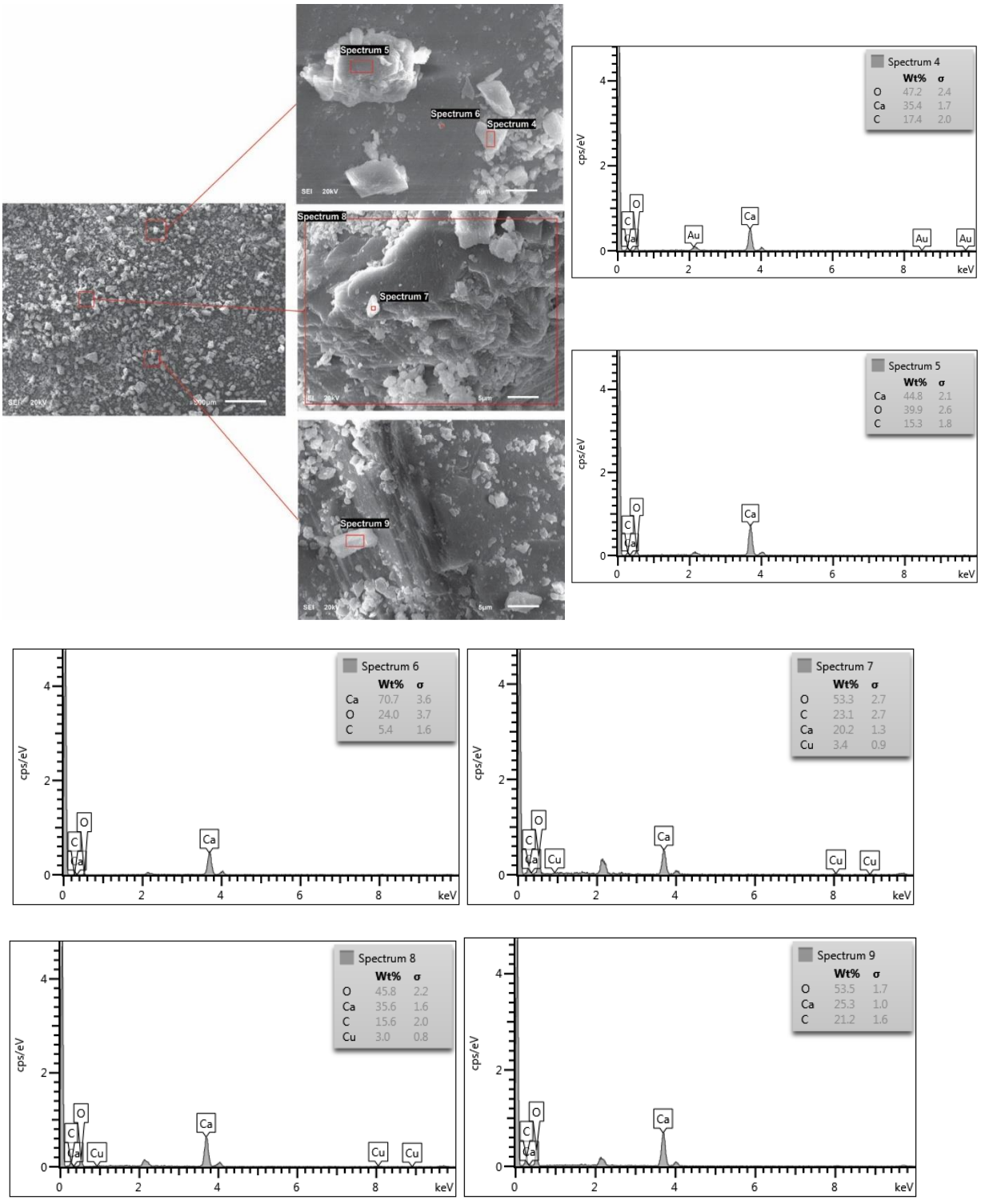

Figure 36: SEM image (top left) and EDS spectra (top right & bottom) modified calcite rock with model oil (TS) and treated with SW0.5NaBr

Table 19: Elemental composition for different spots as highlight in SEM image of modified calcite rock (TS) treated with SW0.5NaBr

Element	Spectrum 4	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8	Spectrum 9
C	17.36	15.27	5.37	23.37	16.61	21.21
O	47.23	39.92	23.97	53.54	46.81	53.54
Ca	35.41	44.81	70.66	20.62	36.57	25.26
Total:	100.00	100.00	100.00	100.00	100.00	100.00

4.26 Surface characterization of modified calcite with model oil (TS) and treated in SW0.5NaI using SEM-EDS

Figure 37 shows the SEM-EDS spectra of calcite rock particles modified with model oil (TS) and treated in SW0.5NaI and Table 20 summarizes the elemental composition obtained by EDS spectra. As we discussed before, if the calcium content is above 40 percent, it can be treated as pure calcite in our case. So, spectrum 10, 11 and 12 shows pure calcite while spectrum 13 and 14 show adsorbed surfaces. It is observed that the addition of NaI in sea water partially removes some stearic acid from the rock surface. As compared to all other brines used in the study, SW0.5NaI is more effective in desorbing adsorbed stearic acid as confirmed by the zeta potential measurements and SEM-EDS spectra. Recently, Valori et al. [134] used a similar composition of ions as presented in SW0.5NaI brine and performed core flood experiments on carbonate rock. They observed a total additional oil recovery of around 15% using SW0.5NaI in secondary mode after sea water (salinity similar to SW) injection.

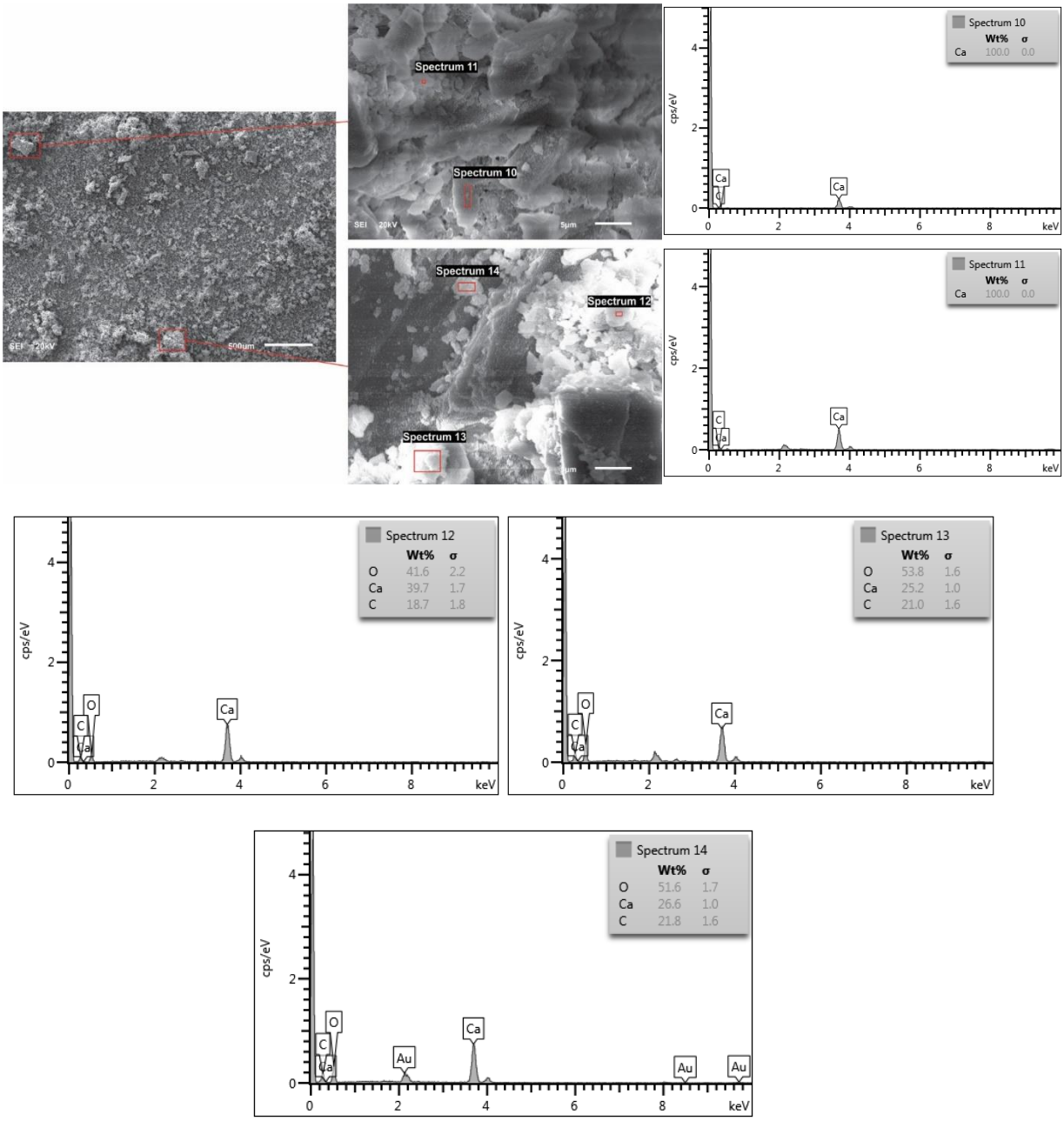

Figure 37: SEM image (top left) and EDS spectra (top right & bottom) modified calcite rock with model oil (TS) and treated with SW0.5NaI

Table 20: Elemental composition for different spots as highlighted in SEM image of modified calcite rock (TS) treated with SW0.5NaI

Element	Spectrum 10	Spectrum 11	Spectrum 12	Spectrum 13	Spectrum 14
C	0.00	0.00	18.66	21.02	21.83
O	0.00	0.00	41.63	53.76	51.61
Ca	100.00	100.00	39.71	25.22	26.56
Total:	100.00	100.00	100.00	100.00	100.00

4.27 Surface characterization of calcite surface using Raman Spectroscope

As shown in Figure 38, we can easily identify two major peaks that are originating at Raman shift of 980 cm^{-1} and 1016 cm^{-1}. Alexander et al. [135] identified that the only detectable peaks in sea water are SO_4^{2-} (980 cm^{-1}) and HCO_3^- (1000 cm^{-1}). He stated that the sulphate peak (980cm^{-1}) is detectable when its concentration is around 1mg/L or higher. Since in our case, the concentration of sulphate in sea water is above 1 mg/L, so it is possible to detect sulphate. According to Wolfram et al. [136], HCO_3^- can be easily identified by its most intense peak at 1016 cm^{-1}, which can be clearly seen in our case. Francis et al. [137] observed that the addition of Na^+ and Mg^{2+} in the presence of SO_4^{2-} does not change Raman spectrum at all and the addition of Na^+ and Mg^{2+} could modify the intensity of the sulphate band at 980 cm^{-1}. Moreover, the very low intensity peak at 662 cm^{-1} that was appeared in only one spectrum can be used to identify calcium ion [138]. Thus, we have identified two ions (SO_4^{2-} and HCO_3^-) in all Raman spectra, while other ions such as calcium, magnesium, sodium and chloride that were present in sea water are not detectable by the Raman spectroscopy, due to the detection limit.

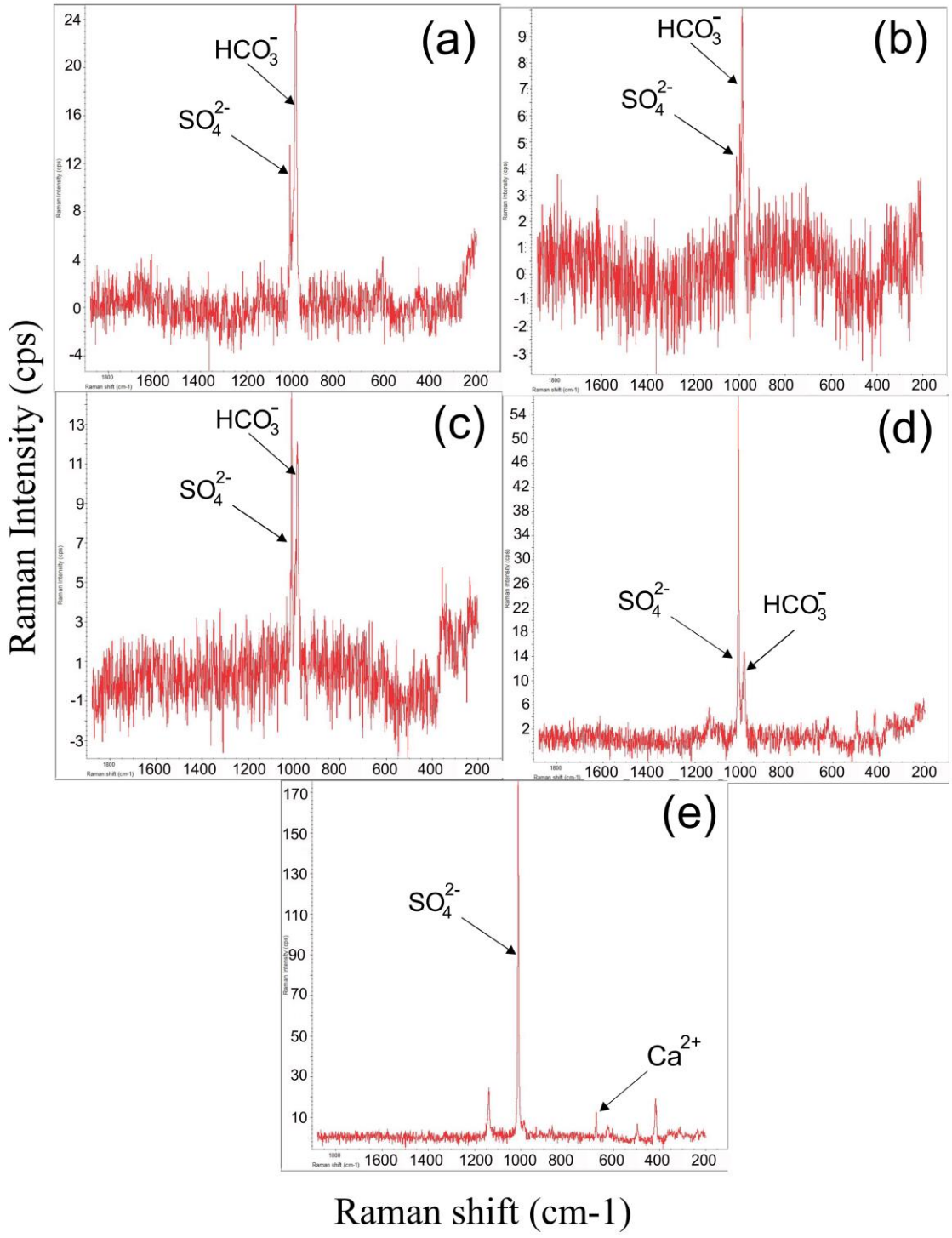

Figure 38: Five different Raman spectra of evaporated Sea water

No intense peak can be observed from Raman spectra of evaporate filtrate after conditioning with modified rock (TS) as shown in Figure 39 except sulphate peak at 980 cm^{-1}. A lot of noise can be seen due to the humidified nature of the sample. The peaks of stearic acid that are usually seen between 1450-1500 cm^{-1} and 1320 cm^{-1} were not observed [138]. The reason behind the non-detectable stearic acid may be the very small concentration of stearic acid or the effect of other ions like SO_4^{2-} and HCO_3^- that could mask the effect of stearic acid.

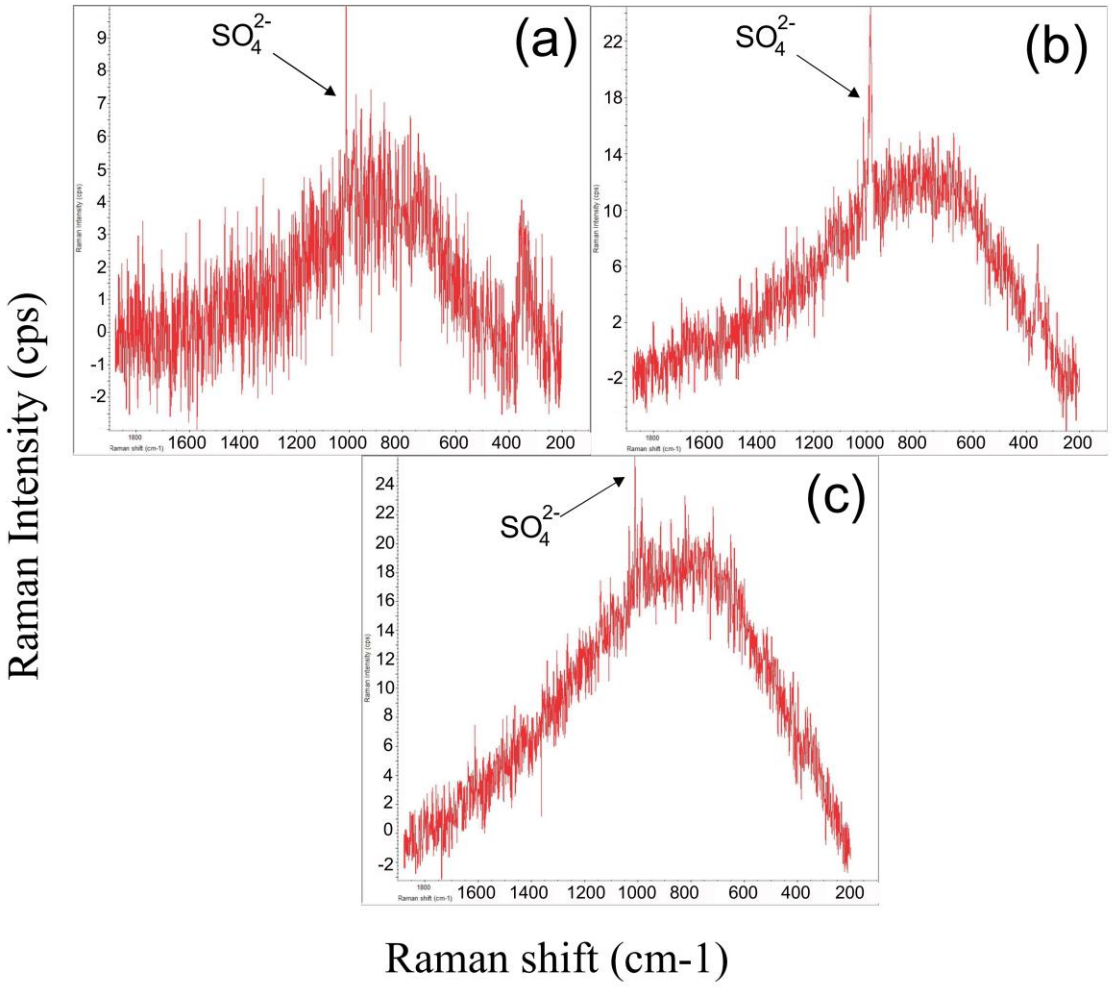

Figure 39: Three different Raman spectra of evaporated filtrate of sea water after treating with modified rock (TS)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of the extensive zeta potential measurements and surface characterization techniques, the following conclusions can be drawn.

1. Zeta potential of calcite and carbonate outcrop is negative in DI water due to preferential leaching of Ca^{2+} ions from the calcium carbonate lattice.

2. The magnitude of the negative zeta potential values is higher in carbonate outcrop as compared to calcite. The possible explanation for the increased negative charge in carbonate outcrop is the silica content that was found in carbonate outcrop which was absent in calcite.

3. The magnitude of negative zeta potential in calcite rock increases when the rock is modified with the model oils (TS, TA and TSA) and then conditioned in DI water, as compared to unmodified calcite rock suspensions in DI water. It is attributed to the adsorption of surface active components from the model oils on the rock surface. This observation is confirmed by the floatation test. Thus, the increase in negative zeta potential indicates the oil wet nature of the rock particles.

4. The magnitude of zeta potential values of calcite rock aged in model oils (TS, TA and TSA) and suspended in DI water are all similar, considering that the model oil (TSA)

contains the same amount of stearic acid and asphaltene as it is present in model oil (TS) and model oil (TA). It is attributed to the competition between stearic acid and asphaltene to adsorb on the sites of calcite surface and the effect of stearic acid and asphaltene is not added up.

5. The magnitude of negative zeta potential in carbonate outcrop increases when the rock is aged with the model oils (TS and TSA) and then conditioned in DI water, as compared to unmodified carbonate outcrop rock conditioned in DI water. However, particles modified with model oil (TA) shows similar ζ as observed with unmodified carbonate outcrop in DI water. Floatation test confirms some adsorption of model oil (TA) on the carbonate outcrop rock surface before conditioning in DI water. This is attributed to the adsorption of asphaltene on carbonate outcrop but released when conditioned in DI water. Results of modified carbonate outcrop (TSA) in DI water also confirms the competition of asphaltene and stearic acid, as the magnitude of zeta potential slightly reduced as compared to model oil (TS).

6. The SEM-EDS spectra showed increasing concentrations of carbon and oxygen elements when calcite rock is modified with model oil (TS) as compared to unmodified or pure calcite rock. It is attributed to the adsorption of surface active component ($\sim COOH^-$) of stearic acid on the surface of calcite rock.

7. All studied brines showed different behavior in modifying the surface rock properties as observed through zeta potential. Conditioning of modified calcite rock particles in low salinity brines (5000 ppm of NaCl, NaBr and NaI, respectively) showed consistent less negative charge as compared to DI water while the effect of 5000 ppm NaI

was most significant. It is attributed to the release of adsorbed model oil components that were causing the increased negative charge.

8. All low salinity brines (5000 ppm of NaCl, NaI or NaBr, respectively) showed less negative charge on the carbonate outcrop rock surface modified with model oils (TS) as compared to the corresponding zeta potential value in DI water. However, the effect of 5000 ppm NaBr was more significant. While for other modified carbonate outcrop particles (TA and TSA), DI water is better in releasing the oil components as compared to low salinity brines.

9. All modified calcite and carbonate outcrop particles showed more negative charge in sea water (SW) and sea water with added 0.5 wt% NaCl (SW0.5NaCl) brine as compared to the modified rock particles in sea water with added 0.5 wt% NaBr (SW0.5NaBr) and sea water with added 0.5 wt% NaI (SW0.5NaI). It is attributed that the conditioning of particles in sea water and SW0.5NaCl did not release polar oil components from the rock surface and the rock particles remained oil wet. Whereas, SW0.5NaBr and SW0.5NaI released oil components from the rock surface, while SW0.5NaI showed more promising results as compared to SW0.5NaBr. Consequently, the desorption of polar oil components leads to make the rock surface less oil wet.

5.2 Recommendations

- Core flooding experiments could be performed using sea water with NaI or NaBr brines at the tertiary mode to confirm their effectiveness in releasing the oil and getting better oil recovery.
- Similar set of zeta potential measurements could also be investigated using different carboxylic groups such as Naphthenic acid, resins etc.
- Similar set of zeta potential measurements could also be investigated using different carbonate minerals such as magnesite, gypsum, anhydrite etc.
- Dead crude oil could also be used along with model oil.
- Different ions could also be investigated such borate, phosphate etc.
- Modeling using geochemical model to investigate surface complexation and to better understand the recovery mechanisms.

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VITAE

Name	: Ahmed Sadeed
Nationality	: Pakistani
Date of Birth	:9/11/1990
Email	: sadeed_saif@hotmail.com
Address	: R-11/D, Gulshan-e-Kaneez Fatima Society, Block 2, Karachi, Pakistan
Academic Background	: **MS (Petroleum Engineering)**
	May, 2017
	King Fahd University of Petroleum and Minerals
	Dhahran, Saudi Arabia
	B.E. (Petroleum Engineering)
	December, 2012
	NED University of Engineering and Technology, NEDUET
	Karachi, Pakistan